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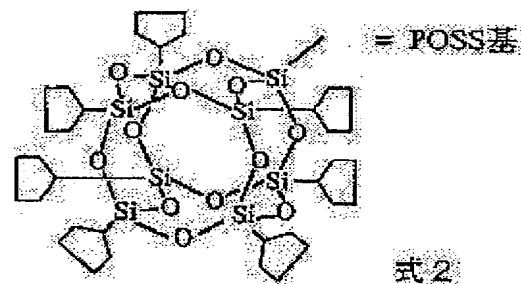
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(54) ION-CONDUCTING FILM AND METHOD OF PRODUCING THE SAME

(57)Abstract:

PROBLEM TO BE SOLVED: To provide an ion-conducting film for a polymeric solid fuel cell, having a methanol-barrier property, heat resistance, high ionic conductivity, mechanical strength, and inexpensiveness, and to provide a method of producing the same.

SOLUTION: This ion-conducting film is formed by combining an ion-conducting resin which comprises an aromatic monomer I, an ion-conducting monomer II, a high-volume monomer III, and a crosslinking agent IV and is expressed by the formula 1 with a fibrous aggregate to form a film. A nonwoven glass fabric is, for example, combined with the ion-conducting resin comprising t-butylstyrene as the component I, 2-acrylamide-2-methylpropanesulfonic acid as the component II, methacryloxypropyl POSS (POSS is expressed by the formula 2) as the component III, and bisphenol A diglycerol ether diacrylate as the component IV.



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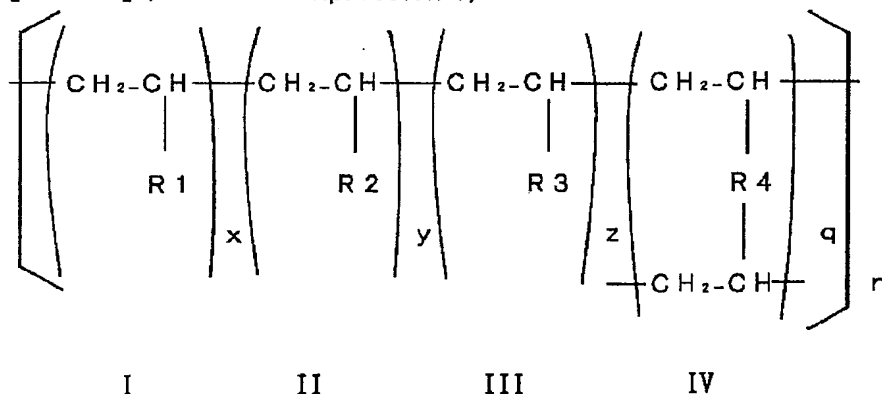
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CLAIMS

[Claim(s)]

[Claim 1] (Structure expression 1)



The aromatic series system monomer I, the ionic conduction system monomer II, and high volume monomer III And ionic conduction film characterized by compounding the ionic conduction resin and the fiber aggregate of the above-mentioned structure expression 1 which consists of a cross linking agent IV in the shape of film.

[Claim 2] Aromatic series system monomer I Consist of an aromatic series system vinyl monomer, and it consists of a vinyl monomer in which the ionic conduction system monomer II has an acidic group. High volume monomer III Boil all, and it is more three-dimensional and consists of any one of silicon-oxygen, silicon-carbon, and the carbon-carbon bondings, or a thing in which the cage configuration was formed. A cross linking agent IV is ionic conduction film according to claim 1 characterized by being compound-ized with the fiber aggregate which consisted of an aromatic series ring and was chosen from among the shape of the shape of the shape of reticulated [of organic fiber or an inorganic fiber], and textile fabrics, and a nonwoven fabric, and fibril.

[Claim 3] Aromatic series system monomer I An R1= carbon number consists of an aromatic series functional group of the necessary number. The ether which permits the case where, as for the ionic conduction system monomer II, an R2= carbon number contains the hydrocarbon part of the necessary number, and the hetero atom of the necessary number, Ester, acrylamide, an amide, an alkyl part, and a sulfonic group, It consists of what has the ionic conduction radical in which any one or all of a phosphoric acid carried out the chemical bond to the shape of a straight chain or a branching straight chain. High volume monomer III Two or more ring compounds surrounded with the silicon or oxygen atom of the necessary number In the cage configuration compound constituted when carrying out silicon-oxygen-silicon association through an oxygen atom in the silicon atoms which face, and connected by silicon-oxygen-silicon association of a necessary number It consists of what has a high functional group. **** which presents the structure in which silicon carried out the chemical bond to the annular aliphatic series system carbon compound of a required-number membered-ring -- A cross linking agent IV consists of an aromatic series ring. These vinyl monomers Copolymerization and the ionic conduction resin which constructed the bridge, a synthetic fiber, or the ceramics, Ionic conduction film according to claim 1 characterized by including the fiber aggregate chosen from among the shape of the shape of the shape of reticulated and textile fabrics which consists of either among glass, a metal, and a nonmetal system element compound, and a nonwoven fabric, and fibril inside the ionic conduction film.

[Claim 4] Aromatic series system monomer I t-butyl styrene and the ionic conduction system monomer II

are 2-acrylamido-2-methyl propane sulfonic acid and the high volume monomer III. Ionic conduction film according to claim 1 characterized by compound-izing a nonwoven glass fabric in the ionic conduction resin propyl methacrylic POSS and whose cross linking agent IV are bisphenol A glycerate diacrylate. [Claim 5] claims 1-4 -- the time of manufacturing the ionic conduction film given in any they are -- aromatic series system monomer I Weight content 5% to 80% High volume monomer III The canal polymerization phase by which an organic solvent is further constituted [0.1% - 50% and a cross linking agent IV] for a hydrophobic polymerization initiator from 1% - 85% of each within the limits 0.01% to 20% 0.02% to 30%, The ionic conduction system monomer II 3% - 90%, The manufacture approach of the ionic conduction film characterized by a hydrophilic polymerization initiator sinking in the fiber aggregate in pickup 20%-520% again to the vinyl monomer solution which consists of a hydrophilic polymerization phase in which water is contained in 6% - 95% of each range 0.03% to 25%.

[Claim 6] claims 1-4 -- the time of manufacturing the ionic conduction film given in any they are -- aromatic series system monomer I Weight content 5% to 80% High volume monomer III The canal polymerization phase by which an organic solvent is further constituted [0.1% - 50% and a cross linking agent IV] for a hydrophobic polymerization initiator from 1% - 85% of each within the limits 0.01% to 20% 0.02% to 30%, After a hydrophilic polymerization initiator sinks [the ionic conduction system monomer II / water] in the fiber aggregate in pickup 20%-520% 3% to 90% again to the hydrophilic polymerization phase contained in 6% - 95% of each range 0.03% to 25%, The manufacture approach of the ionic conduction film characterized by making it stick to a fiber aggregate using a synthetic-resin film, irradiating bridge formation energy at a fiber aggregate, and carrying out the polymerization of a vinyl monomer and the cross linking agent.

[Claim 7] A conductor, infrared radiation, Depending on any of far-infrared irradiation equipment they are The ultraviolet radiation or the light exposure machine of the range of the conditions maintained for 0.5 seconds to 4 hours in the range whose vinyl monomer impregnation temperature of a fiber aggregate is 35 degrees C - 220 degrees C, or 190nm - 700nm wavelength is used. A vinyl monomer impregnation body surface 0.5 mW/cm² From to 5600mW/cm² Exposure conditions which become a light-receiving energy range, Or the manufacture approach of the ionic conduction film according to claim 6 characterized by carrying out the bridge formation energy exposure of the electron ray on the conditions irradiated for 0.2 seconds to 5 hours in the range of 20 Mrad-m/min to 360 Mrad-m/min with electron-beam-irradiation equipment.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the ionic conduction film which has high ion conductivity, thermal resistance, and methanol barrier nature, and its manufacture approach.

[0002]

[Description of the Prior Art] While the measure for problem solvings, such as air pollution and global warming, is cried for, the expectation for development of an exhaust gas control mold automobile shows the rise. Especially a polymer electrolyte fuel cell has various advantages, like energy overall efficiency is high and environment nature is high, and its expectation is great as a clean new generation-of-electrical-energy format for electric vehicles. The generation-of-electrical-energy method generally called a fuel cell takes out the energy which fuels (hydrogen etc.) have using the reverse reaction of electrolysis of water as direct electrical energy. Generally it is represented by four kinds, a phosphoric-acid mold, a melting carbonate mold, a solid oxide type, and a solid-state macromolecule mold, from the description on a configuration.

[0003] As ionic conduction film used for the polymer electrolyte fuel cell (PEFC) of the inside represented by said four kinds, the ionic conduction film of the mold of perfluoroalkyl sulfonic acids, such as a trade name "Nafion", non-constructing a bridge has been used.

[0004]

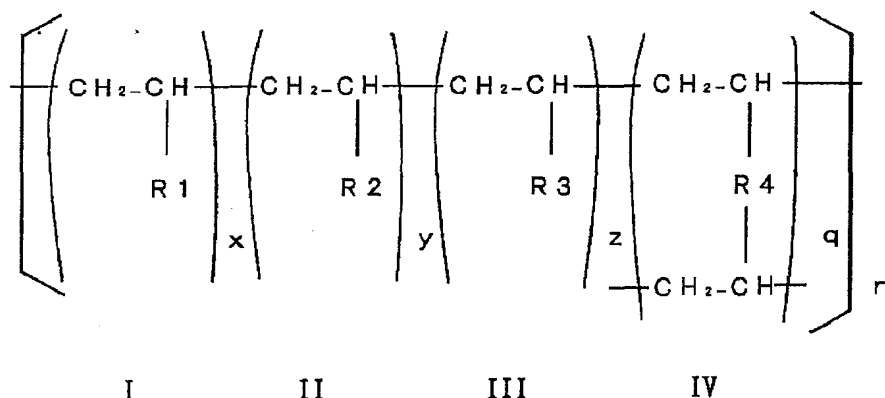
[Problem(s) to be Solved by the Invention] The above-mentioned fluorine system ionic conduction film has high chemical stability and thermal resistance, and in order to raise the practicability of a polymer electrolyte fuel cell, it has played the important role. However, the fluorine system ionic conduction film used conventionally was developed as a diaphragm at the time of electrolyzing salt originally and taking out caustic alkali of sodium and chlorine gas on industrial level, and it was not developed as an ingredient for fuel cells, since membrane resistance is large, it is pointed out that the generation-of-electrical-energy energy efficiency of a fuel cell is falling, and many improving points are left behind as a technical problem.

[0005] Moreover, the approach of adding a function required as a direct methanol mold fuel cell additionally, and going is adopted in many cases, copying the predominance of a large number which the fluorine system ionic conduction film has also in the field of the fundamental research of a direct methanol mold fuel cell (DMFC). As these functions, although it is 1 methanol barrier property, 2 thermal resistance, 3 ion conductivity, 4 dynamic reinforcement, 5 low-price nature, etc., when all of these functions are related, one function is raised in these and it goes, there is an inclination for other functions to fall. For example, in the case of a direct methanol mold fuel cell, in the actual condition, since catalytic activity is low, the operation temperature of a cell must be set as a temperature requirement high to 130 degrees C - 200 degrees C. However, the oxidative degradation of cutting of a polymer principal chain occurring under the high effect of acid which a sulfonic group has in the film conventionally happens. Furthermore, active jamming of the reduction reaction in the cathode resulting from a methanol crossover takes place, and the generation efficiency of a cell falls. Therefore, it is a technical problem to raise the above-mentioned function with sufficient balance.

[0006] The object of this invention is offering the ionic conduction film which has methanol barrier property, thermal resistance, high ion conductivity, dynamic reinforcement, and low-price nature, and its manufacture approach in view of the above-mentioned technical problem.

[0007]

[Means for Solving the Problem] Ionic conduction film by this invention for attaining the above-mentioned object (structure expression 1),



The aromatic series system monomer I, the ionic conduction system monomer II, and high volume monomer III And it is characterized by compounding the ionic conduction resin and the fiber aggregate of the above-mentioned structure expression 1 which consists of a cross linking agent IV in the shape of film.

[0008] Moreover, the aforementioned aromatic series system monomer I It consists of an aromatic series system vinyl monomer. It consists of a vinyl monomer in which the ionic conduction system monomer II has an acidic group. High volume monomer III Boil all, and it is more three-dimensional and consists of any one of silicon-oxygen, silicon-carbon, and the carbon-carbon bondings, or a thing in which the cage configuration was formed. It is characterized by compound-izing a cross linking agent IV with the fiber aggregate which consisted of an aromatic series ring and was chosen from among the shape of the shape of the shape of reticulated [of organic fiber or an inorganic fiber], and textile fabrics, and a nonwoven fabric, and fibril.

[0009] Furthermore, the aforementioned aromatic series system monomer I An R1= carbon number consists of an aromatic series functional group of the necessary number. The ether which permits the case where, as for the ionic conduction system monomer II, an R2= carbon number contains the hydrocarbon part of the necessary number, and the hetero atom of the necessary number, Ester, acrylamide, an amide, an alkyl part, and a sulfonic group, It consists of what has the ionic conduction radical in which any one or all of a phosphoric acid carried out the chemical bond to the shape of a straight chain or a branching straight chain. High volume monomer III Two ring compounds surrounded with the silicon or oxygen atom of the necessary number In the cage configuration compound constituted when carrying out silicon-oxygen-silicon association through an oxygen atom in the silicon atoms which face, and connected by silicon-oxygen-silicon association of a necessary number It consists of what has a high functional group. **** which presents the structure in which silicon carried out the chemical bond to the annular aliphatic series system carbon compound of a required-number membered-ring -- A cross linking agent IV consists of an aromatic series ring. These vinyl monomers Copolymerization and the ionic conduction resin which constructed the bridge, a synthetic fiber, or the ceramics, It is characterized by including the fiber aggregate chosen from among the shape of the shape of the shape of reticulated and textile fabrics which consists of either among glass, a metal, and a nonmetal system element compound, and a nonwoven fabric, and fibril inside the ionic conduction film.

[0010] It is said aromatic series system monomer I further again. t-butyl styrene and the ionic conduction system monomer II are 2-acrylamido-2-methyl propane sulfonic acid and the high volume monomer III. It is characterized by compound-izing a nonwoven glass fabric in the ionic conduction resin propyl methacrylic POSS and whose cross linking agent IV are bisphenol A glycerate diacrylate.

[0011] The manufacture approach of the above-mentioned ionic conduction film is the aromatic series system monomer I. Weight content 5% - 80%, High volume monomer III The canal polymerization phase by which an organic solvent is further constituted [0.1% - 50% and a cross linking agent IV] for a hydrophobic polymerization initiator from 1% - 85% of each within the limits 0.01% to 20% 0.02% to 30%, The ionic conduction system monomer II 3% - 90%, A hydrophilic polymerization initiator is characterized by sinking in the fiber aggregate in pickup 20%-520% to the vinyl monomer solution which consists of a hydrophilic polymerization phase in which water is contained in 6% - 95% of each range 0.03% to 25% again. In addition, as a hydrophobic polymerization initiator, although azobisisobutyronitril, a benzophenone, benzoyl peroxide, peroxidation t-butyl, etc. are mentioned, it is not limited to these initiators. As a hydrophilic polymerization initiator, although ammonium-peroxydisulfate, potassium-peroxydisulfate, peroxydisulfuric-acid sodium, 2, and 2-azobis [2-(2-imidazoline-2-IRU) propane] dihydrochloride etc. is mentioned, it is not limited to especially these initiators.

[0012] Moreover, other manufacture approaches of the above-mentioned ionic conduction film are the aromatic series system monomers I. Weight content 5% – 80%, High volume monomer III The canal polymerization phase by which an organic solvent is further constituted [0.1% – 50% and a cross linking agent IV] for a hydrophobic polymerization initiator from 1% – 85% of each within the limits 0.01% to 20% 0.02% to 30%, After a hydrophilic polymerization initiator sinks [the ionic conduction system monomer II / water] in the fiber aggregate in pickup 20%–520% 3% to 90% again to the hydrophilic polymerization phase contained in 6% – 95% of each range 0.03% to 25%, It is characterized by making it stick to a fiber aggregate using a synthetic-resin film, irradiating bridge formation energy at a fiber aggregate, and carrying out the polymerization of a vinyl monomer and the cross linking agent.

[0013] The approach of irradiating the fiber aggregate the above-mentioned bridge formation energy A conductor, infrared radiation, Depending on any of far-infrared irradiation equipment they are The ultraviolet radiation or the light exposure machine of the range of the conditions maintained for 0.5 seconds to 4 hours in the range whose vinyl monomer impregnation temperature of a fiber aggregate is 35 degrees C – 220 degrees C, or 190nm – 700nm wavelength is used. A vinyl monomer impregnation body surface 0.5 mW/cm² From to 5600mW/cm² Exposure conditions which become a light-receiving energy range, Or it is characterized by carrying out the bridge formation energy exposure of the electron ray on the conditions irradiated for 0.2 seconds to 5 hours in the range of 20 Mrad-m/min to 360 Mrad-m/min with electron-beam-irradiation equipment.

[0014]

[Embodiment of the Invention] The example of this invention is explained based on a drawing below. About a drawing, the giant-molecule structure of the fluorine system ionic conduction film and drawing 2 drawing 1 The hydrophilic-non-dense aqueous-phase model inside the fluorine system film, The amelioration effectiveness of demand characteristics [in / drawing 3 / the structure of a POSS radical, and drawing 4 , and / in drawing 5 / an example 1], [a methanol expulsive measurement cel] The relation of the weight content of an aromatic series system monomer and an ionic conduction value, [in / in drawing 6 / example 2.] The relation of the weight content of a methanol expulsive radical and film reinforcement, [in / in drawing 7 / an example 3] The relation of the weight content of a cross linking agent and film reinforcement, the relation of the weight content of a polymerization initiator and an ionic conduction value, [in / in drawing 8 / an example 4] [in / in drawing 9 / an example 5] The relation of the weight content of an organic solvent and a methanol expulsive value, [in / in drawing 10 / an example 6] The relation of the polymerization content of an ionic conduction system monomer and an ionic conduction value, [in / in drawing 11 / an example 7] The relation of the weight content of a hydrophilic polymerization initiator and a heat-resistant value, [in / in drawing 12 / an example 8] The relation of the weight content of water and a heat-resistant value, the relation of a pickup and an ionic conduction value, [in / in drawing 13 / an example 9] [in / in drawing 14 / an example 10] The relation of curing temperature and film reinforcement, the relation of the setting time and a methanol abatement value, [in / in drawing 15 / an example 11] [in / in drawing 16 / an example 12] The relation between ultraviolet-visible-ray wavelength [in / in drawing 17 / an example 13], and film reinforcement, the relation of a light-receiving energy density and an ionic conduction value, [in / in drawing 18 / an example 14] The relation of an electron ray reinforcement and a heat-resistant value and drawing 20 show the relation of the light-receiving energy density and ionic conduction value in an example 16. [in / in drawing 19 / an example 15]

[0015] in addition, said aromatic series system monomer I in claim 3 An R1= carbon number consists of an aromatic series functional group to 1–20 pieces. The concrete example of this Styrene, 3-methyl styrene, 4-methyl styrene, t-butyl styrene, sec-butyl styrene, Alpha methyl styrene, trans-beta-methyl styrene, 2-chloro styrene, Although it is 3-chloro styrene, 4-chloro styrene, 2-vinyl naphthalene, 9-vinyl anthracene, a vinyl pyrene, N-vinylcarbazole, 2-vinylpyridine, 4-vinylpyridine, or 1-vinyl imidazole, it is not limited to these. The ether which permits the case where, as for the ionic conduction system monomer II, an R2= carbon number contains the hydrocarbon part to 1–18 pieces, and the hetero atom to 1–5 pieces, Ester, acrylamide, an amide, an alkyl part, and a sulfonic group, It consists of what has the ionic conduction radical in which any one or all of a phosphoric acid carried out the chemical bond to the shape of a straight chain or a branching straight chain. The concrete example of this 2-acrylamido-2-methyl propane sulfonic acid, Although it is 4-styrene sulfonic-acid sodium, sodium allylsulfonate, sodium methallylsulfonate, a vinyl sulfonic acid, a vinyl propane sulfonic acid, ethyl diethyl phosphono acetate, a vinyl phosphoric acid, an allyl compound phosphoric acid, etc. It is not limited to these compounds. High volume monomer III Two ring compounds surrounded with the silicon or oxygen atom to 3–80 pieces In the cage configuration compound constituted when carrying out silicon-oxygen-silicon association through an oxygen atom in the silicon atoms which face, and connected by silicon-oxygen-silicon association of 3–80 It consists of what has a

high functional group. **** which presents the structure in which silicon carried out the chemical bond to the annular aliphatic series system carbon compound of three to 12 membered-ring -- For example, although propyl methacrylic POSS, Vinyl POSS, POSS acrylamide, an allyl compound POSS, Metallyl POSS, methacrylic one POSS, acrylic-acid POSS, etc. are mentioned, it is not limited to these compounds. A cross linking agent IV is not limited to these cross linking agents, although it consists of an aromatic series ring and bisphenol A glycerate diacrylate, a divinylbenzene, divinyl naphthalene, diallyl phthalate, diaryl tetrabromo phthalate, a diaryl diphenyl silane, diaryl diphenylphosphine, etc. are mentioned as a concrete example of this. The fiber aggregate chosen from among the shape of the shape of the shape of reticulated [which these vinyl monomers become from either among copolymerization and the ionic conduction resin which constructed the bridge, a synthetic fiber or the ceramics, glass a metal, and a nonmetal system element compound], and textile fabrics, and a nonwoven fabric, and fibril is included inside the ionic conduction film. Although each numerical range of the carbon number of the . above R1 and R2 which is not what is restricted to these compounds although it is silicon carbide, boron carbide, silicon nitride, boron nitride, etc. as a nonmetal system element compound, the silicon of R3 or the oxygen atom number, a silicon-oxygen-silicon joint number, and the number of membered-rings of silicon is desirable range, it is not necessarily limited to each of this numerical range.

[0016]

[Example 1] The ionic conduction film was obtained by dissolving t-butyl styrene 5.25g, 0.8g of 2-acrylamido-2-methyl propane sulfonic acid, propyl methacrylic POSS0.25g, and bisphenol A glycerate diacrylate 1.0g in N and N'-dimethylformamide 8ml and the mixed solvent of 3ml of water, and carrying out heating bridge formation of the solution which added azobisisobutyronitril 20mg and was obtained at 10 degrees C for 3 minutes using a hot calender roll, after sinking into the polypropylene network of 20 meshes at pickup 250%. In addition, the structure of a POSS radical is as being shown in drawing 3 .

[0017] The methanol abatement engine performance of the ionic conduction film obtained the account of a top was measured as follows. That is, in the cel configuration for measurement shown in drawing 4 , two glass cylinders with doubling cost with a methanol permeability width of face of 10mm (98ml of inner capacity) were prepared, the ionic conduction film with a diameter of 70mm was put between them, the methanol transparency diameter of the ionic conduction film was set to 50mm, 3% of the weight of the methanol water solution was put into the interior of one glass cylinder (methanol phase), and the interior of another glass cylinder was filled up with aqua destillata (aqueous phase). After setting the time of finishing setting up these measurement cels as measurement initiation and sampling water in part from the aqueous phase after 30-minute progress, it analyzed using the Hitachi G-5000 mold gas chromatograph (FID detector), and the quantum of the methanol concentration Mi in the aqueous phase was carried out.

[0018] When considering as the methanol concentration Mf similarly measured using the fluorine system ionic conduction film (example of a comparison), it was defined as the following formula (1) by making a methanol transparency control value into a relative value.

Methanol abatement value = Mf/Mi -- Formula (1)

As the result was shown in drawing 5 , compared with the fluorine system ionic conduction film (example of a comparison) used as ionic conduction film of a direct methanol mold fuel cell, the ionic conduction film by this invention showed higher methanol expulsive conventionally.

[0019] About thermal resistance, it evaluated as follows. The part was sampled from said obtained ionic conduction film, and the pyrolysis initiation temperature Ti of the ionic conduction film was measured in air using TG-DTA. The pyrolysis initiation temperature Tf of the conventional fluorine system ionic conduction film was measured similarly, and the definition was given as a relative value of the value the fluorine system film indicates thermal resistance to be like the following formula (2).

A heat-resistant value = Ti/Tf -- Formula (2)

As the result was shown in drawing 5 , the heat-resistant value of the ionic conduction film by this invention was larger than the value of the fluorine system film which is film conventionally, and showed higher thermal resistance.

[0020] About ion conductivity, it evaluated as follows. It stuck on fluororesin plate manufacturing so that *****, 1.0cm long, 2.5cm wide, and the platinum foil with a thickness of 10 microns might be prepared in the center section of 4.0cm long, 4.0cm wide, and fluororesin plate manufacturing with a thickness of 0.5cm and the 1.0cm side of the platinum foil might touch 0.5cm long and a 1.0cm wide sump to 1.0cm [about] of the sump of fluororesin plate manufacturing in it.

[0021] After producing these two plates, it dips in 1/40-N nitric-acid water solution of chloroplatinic acid, and they are bath voltage 3.0V and current density 40 mA/cm². Platinum black was plated on the platinum foil for 1 hour. This fluororesin plate manufacturing was dipped into 1% sulfuric acid, the platinum electrode

was used for the counter electrode, and each of the fluororesin plate manufacturing of two sheets was followed in the actuation which energizes a platinum-electrode side for 10 minutes in electrical-potential-difference 3.0V by using the platinum-foil side of a negative electrode and fluororesin plate manufacturing as a positive electrode.

[0022] thus, the ionic conduction film cut into 1.0cm long and 1.5cm wide between two fluororesin plate manufacturing of obtained platinum black plating -- inserting -- the platinum foil -- solar TRON company make -- it connected with impedance analyzer S1-1260, and membranous ionic conductivity was computed with the alternating current anodizing process. The ionic conduction value by this invention was defined like the following formula (3).

Ionic conduction value = I_i/I_f -- Formula (3)

If: ionic conductivity I_i of the conventional fluorine system -- the degree of ionic conduction of the film by this invention -- as the result was shown in drawing 5, also in ion conductivity, it became clear that the ionic conduction film by this invention is conventionally larger than membranous ion conductivity.

[0023] About membranous reinforcement, it evaluated as follows. the stress at the time of pulling 15cm long and the 0.5cm wide ionic conduction film, hanging on a testing machine, and making a sample fracture by hauling in the distance between chucks of 10cm -- the cross section of the ionic conduction film -- **** -- when setting tensile strength of S_i and the conventional fluorine system film to S_f for tensile strength by things, film reinforcement was defined like a formula (4). film = on the strength -- a S_i/S_f -- type (4) -- as the result was shown in drawing 5, the film reinforcement by this invention had high film reinforcement compared with the conventional fluorine system film.

[0024]

[Example 2] As the result of having measured the ionic conduction value at the time of changing the weight content of t-butyl styrene at the time of preparing the ionic conduction film in an example 1 is shown in drawing 6, in the range whose t-butyl styrene weight content is 5% - 80%, the ionic conduction value is large compared with the film conventionally, and the range indicated to claim 5 is suitable for the weight content of an aromatic series system monomer.

[0025]

[Example 3] Since film reinforcement is conventionally larger than a membranous value in the range whose weight content propyl methacrylic [POSS] is 0.1% - 50% as drawing 7 shows the film reinforcement when changing weight content propyl methacrylic [POSS] in case the ionic conduction film is prepared in an example 1, the range indicated to claim 5 is appropriate to the weight content of a high volume monomer.

[0026]

[Example 4] In case the ionic conduction film is prepared in an example 1, as drawing 8 shows the film change on the strength at the time of changing the weight content of bisphenol A guru cello rate diacrylate as a cross linking agent, it is conventionally larger than a membranous value in 0.02% - 30% of range, and the range indicated to claim 5 is suitable.

[0027]

[Example 5] Since the weight content of a hydrophobic polymerization initiator is larger than the value of the conventional fluorine system film in the range which is 0.01% - 20% as drawing 9 shows the ionic conduction value when changing the weight content of azobisisobutyronitril as a hydrophobic polymerization initiator in an example 1, the range which indicated the weight content of a hydrophobic polymerization initiator to claim 5 is appropriate.

[0028]

[Example 6] When preparing the ionic conduction film in an example 1, as drawing 10 shows the relation between the weight content of an organic solvent, and a methanol abatement value, the methanol abatement value is conventionally larger than a membranous value at the time of 1% - 85% of range, and, as for the weight content of an organic solvent, the range which indicated the weight content of an organic solvent to claim 5 is appropriate.

[0029]

[Example 7] When preparing the ionic conduction film in an example 1, as drawing 11 shows the relation between the weight content of 2-acrylamido-2-methyl propane sulfonic acid, and an ionic conduction value as an ionic conduction system monomer, in the ionic conduction value, the ionic conduction value is conventionally larger than the film at the time of 3% - 90% of range, and, as for the weight content of 2-acrylamido-2-methyl propane sulfonic acid, the range indicated to claim 5 is suitable for the weight content of an ionic conduction system monomer.

[0030]

[Example 8] In case the ionic conduction film is manufactured in an example 1, as the heat-resistant value

when changing the weight content of a ** RUOKISONI ammonium sulfate as a hydrophilic polymerization initiator is shown in drawing 12, in the heat-resistant value, the weight content of a ** RUOKISONI ammonium sulfate is larger than the value of the conventional fluorine system film at 0.03% – 25% of within the limits, and the range indicated to claim 5 is suitable for the weight content of a hydrophilic polymerization initiator.

[0031]

[Example 9] In case the ionic conduction film is manufactured in an example 1, as drawing 13 shows the heat-resistant value when changing the weight content of water, thermal resistance is conventionally larger than the film in 6% – 95% of range, and, as for the weight content of water, the range indicated to claim 5 is suitable for the weight content of water.

[0032]

[Example 10] When manufacturing the ionic conduction film in an example 1, in case the polypropylene network which is the fiber aggregate is sunk into a monomer solution phase, as the relation between pickup and an ionic conduction value is shown in drawing 14, the range where pickup indicated the pickup of the fiber aggregate to claim 5 by the ionic conduction value being conventionally larger than the film in 20% – 520% of range is appropriate.

[0033]

[Example 11] When making it harden according to the fiber aggregate and bridge formation which sank in the vinyl monomer solution in the example 1, as drawing 15 shows the reinforcement of the ionic conduction film when changing curing temperature, curing temperature is conventionally larger than a membranous value in 35 degrees C – 220 degrees C, and the range indicated to claim 7 is suitable for curing temperature.

[0034]

[Example 12] As the methanol abatement value which the ionic conduction film when changing the setting time of the ionic conduction film in an example 1 shows is shown in drawing 16, the setting time is conventionally larger than membranous physical properties in the range of 0.5 seconds – 4 hours, and the range indicated to claim 7 is suitable for the setting time.

[0035]

[Example 13] When the content of combination which changed the azobisisobutyronitril of a hydrophobic polymerization initiator to the benzophenone is adopted among the monomer solution in an example 1 and a black light is used instead of a hot calender roll, about film reinforcement, as shown in drawing 17, the wavelength of ultraviolet rays is conventionally larger than a membranous value in the range which is 190nm – 700nm, and the range indicated to claim 7 is suitable for the wavelength of the ultraviolet rays by the black light.

[0036]

[Example 14] when changing the light-receiving energy density of the ultraviolet-visible ray which a vinyl monomer impregnation body surface receives in an example 13, the ionic conduction value change of the ionic conduction film is shown in drawing 18 -- as -- a light-receiving energy density -- 0.5 mW/cm² from -- 5600 mW/cm² Membranous ion conductivity is conventionally excelled in the range, and the range which indicated the light-receiving energy density to claim 7 is suitable.

[0037]

[Example 15] Since the thermal resistance which the ionic conduction film shows became conventionally larger than the film when the heat-resistant value of the ionic conduction film when changing the exposure energy of the electron ray at the time of using electron-beam-irradiation equipment instead of an ultraviolet ray lamp in an example 13 irradiated an electron ray in the range of 20 Mrad-m/min – 30 Mrad-m/min, as shown in drawing 19, the range which indicated the exposure energy of the electron ray by electron-beam-irradiation equipment to claim 7 is suitable.

[0038]

[Example 16] The ionic conduction value of the ionic conduction film when changing the irradiation time of an electron ray in an example 15 has exceeded the membranous value conventionally in 0.2 seconds – 5 hours, as shown in drawing 20, and the range indicated to claim 7 is suitable for the irradiation time of the electron ray by electron-beam-irradiation equipment.

[0039] By the way, in a direct methanol mold fuel cell (DMFC), a methanol crossover is an important problem. It is said that a methanol checks electrode catalytic reaction by permeating the inside of the ionic conduction film from an anode (a negative electrode, fuel electrode), and permeating a cathode (a positive electrode, oxygen pole) with moisture. The main electrode reaction in DMFC is as follows.

anode: -- $\text{CH}_3\text{OH} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 6\text{H}^+ + 6\text{e}^-$ cathode: -- since $0.5\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{O}$, among these the

methanol which has permeated check the reduction reaction of a cathode, the output as the whole DMFC, i.e., the generation efficiency of a cell, will decline.

[0040] Then, this invention controlled diffusion of the methanol in the film by introducing a methanol expulsive functional group into the macromolecule structure which forms the ionic conduction film. As shown in drawing 3, the POSS radical which is heptacyclo pentyl PENTASHIKUROOKUTA siloxane 1-IRU as a methanol expulsive functional group was introduced. The structure of drawing 3 has the form in which two annular silicates carried out the chemical bond (Si-O-Si). The methanol molecule which diffuses the inside of the film takes some moisture with it, and forms the methanol water molecule ensemble. Since said POSS radical is having cage configuration structure, these methanols water molecule ensemble is incorporated in a cage.

[0041] Next, silicon belongs to the category with high hydrophobicity and an atomic radius quite small in about 0.04nm and an element, and also has high hydrophobicity (oleophilic), and hydrophobicity has localized it. Hydrophobicity is large although methanol molecules are very few [the part of a methyl group] differences than water. Then, since the methanol water molecule incorporated in said cage is attracted by the hydrophobic-hydrophobic interaction, delay arises at the rate which escapes from a POSS radical rather than a water molecule. Consequently, the diffusion in the film is controlled by the cage effect and the hydrophobic localization effectiveness that a POSS radical has a methanol molecule. In addition, a POSS radical can raise the hydrophobicity in the film, without raising the hydrophobicity of the whole ionic conduction film, since hydrophobicity is carrying out localization.

[0042] About the design of the polymer molecule for using for the ionic conduction film of DMFC, in the fluorine system film used for conventional PEFC and conventional DMFC, compatibility of a fluorine with a methanol is fundamentally large, and the effectiveness which controls a crossover can seldom be expected. Therefore, the raw material (monomer) of a hydrocarbon system was used in the molecular design of these polymers.

[0043] t-butyl styrene was chosen as indicated to claim 4 as an example of the structural material. This t-butyl styrene has the more large hydrophobicity of a monomer. Therefore, since a larger hydrophobic-hydrophobic interaction is expectable, membrane structure can be strengthened more. Moreover, the biphenol A type was used for the cross linking agent. The structure of this cross linking agent has bonding strength high in a polymer generally. Therefore, bridge formation reinforcement and thermal resistance are held by these.

[0044] In addition, the ionic conduction film by this invention can be applied to the flat panel of an electrochemistry type sensor, a light emitting device, and a laptop computer etc. other than a polymer electrolyte fuel cell.

[0045]
[Effect of the Invention] As mentioned above, according to this invention, it has high methanol expulsive and thermal resistance, the physical properties of the film by big ion conductivity, film reinforcement, curing temperature, and the setting time etc. are acquired with sufficient balance, and the ionic conduction film which raised the generation-of-electrical-energy energy efficiency of a fuel cell can be offered by the low price.

[Translation done.]

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TECHNICAL FIELD

[Field of the Invention] This invention relates to the ionic conduction film which has high ion conductivity, thermal resistance, and methanol barrier nature, and its manufacture approach.

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PRIOR ART

[Description of the Prior Art] While the measure for problem solvings, such as air pollution and global warming, is cried for, the expectation for development of an exhaust gas control mold automobile shows the rise. Especially a polymer electrolyte fuel cell has various advantages, like energy overall efficiency is high and environment nature is high, and its expectation is great as a clean new generation-of-electrical-energy format for electric vehicles. The generation-of-electrical-energy method generally called a fuel cell takes out the energy which fuels (hydrogen etc.) have using the reverse reaction of electrolysis of water as direct electrical energy. Generally it is represented by four kinds, a phosphoric-acid mold, a melting carbonate mold, a solid oxide type, and a solid-state macromolecule mold, from the description on a configuration.

[0003] As ionic conduction film used for the polymer electrolyte fuel cell (PEFC) of the inside represented by said four kinds, the ionic conduction film of the mold of perfluoroalkyl sulfonic acids, such as a trade name "Nafion", non-constructing a bridge has been used.

[Translation done.]

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EFFECT OF THE INVENTION

[Effect of the Invention] As mentioned above, according to this invention, it has high methanol expulsive and thermal resistance, the physical properties of the film by big ion conductivity, film reinforcement, curing temperature, and the setting time etc. are acquired with sufficient balance, and the ionic conduction film which raised the generation-of-electrical-energy energy efficiency of a fuel cell can be offered by the low price.

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TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] The above-mentioned fluorine system ionic conduction film has high chemical stability and thermal resistance, and in order to raise the practicability of a polymer electrolyte fuel cell, it has played the important role. However, the fluorine system ionic conduction film used conventionally was developed as a diaphragm at the time of electrolyzing salt originally and taking out caustic alkali of sodium and chlorine gas on industrial level, and it was not developed as an ingredient for fuel cells, since membrane resistance is large, it is pointed out that the generation-of-electrical-energy energy efficiency of a fuel cell is falling, and many improving points are left behind as a technical problem. [0005] Moreover, the approach of adding a function required as a direct methanol mold fuel cell additionally, and going is adopted in many cases, copying the predominance of a large number which the fluorine system ionic conduction film has also in the field of the fundamental research of a direct methanol mold fuel cell (DMFC). As these functions, although it is 1 methanol barrier property, 2 thermal resistance, 3 ion conductivity, 4 dynamic reinforcement, 5 low-price nature, etc., when all of these functions are related, one function is raised in these and it goes, there is an inclination for other functions to fall. For example, in the case of a direct methanol mold fuel cell, in the actual condition, since catalytic activity is low, the operation temperature of a cell must be set as a temperature requirement high to 130 degrees C - 200 degrees C. However, the oxidative degradation of cutting of a polymer principal chain occurring under the high effect of acid which a sulfonic group has in the film conventionally happens. Furthermore, active jamming of the reduction reaction in the cathode resulting from a methanol crossover takes place, and the generation efficiency of a cell falls. Therefore, it is a technical problem to raise the above-mentioned function with sufficient balance.

[0006] The object of this invention is offering the ionic conduction film which has methanol barrier property, thermal resistance, high ion conductivity, dynamic reinforcement, and low-price nature, and its manufacture approach in view of the above-mentioned technical problem.

[Translation done.]

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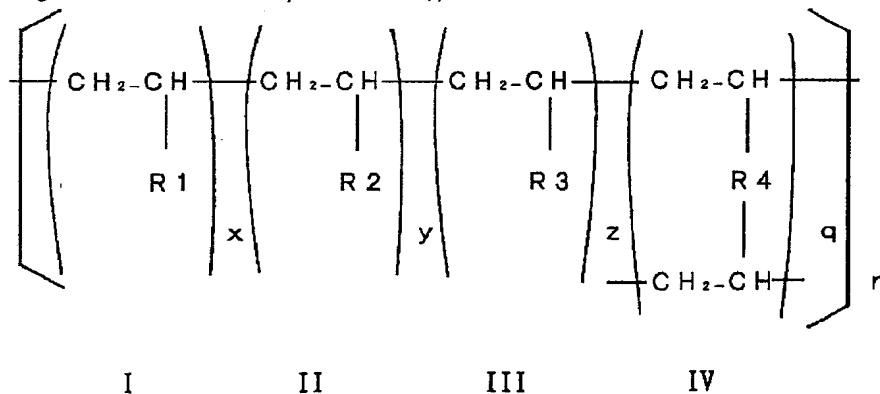
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MEANS

[Means for Solving the Problem] Ionic conduction film by this invention for attaining the above-mentioned object (structure expression 1),



The aromatic series system monomer I, the ionic conduction system monomer II, and high volume monomer III And it is characterized by compounding the ionic conduction resin and the fiber aggregate of the above-mentioned structure expression 1 which consists of a cross linking agent IV in the shape of film.

[0008] Moreover, the aforementioned aromatic series system monomer I It consists of an aromatic series system vinyl monomer. It consists of a vinyl monomer in which the ionic conduction system monomer II has an acidic group. High volume monomer III Boil all, and it is more three-dimensional and consists of any one of silicon-oxygen, silicon-carbon, and the carbon-carbon bondings, or a thing in which the cage configuration was formed. It is characterized by compound-izing a cross linking agent IV with the fiber aggregate which consisted of an aromatic series ring and was chosen from from among the shape of the shape of the shape of reticulated [of organic fiber or an inorganic fiber], and textile fabrics, and a nonwoven fabric, and fibril.

[0009] Furthermore, the aforementioned aromatic series system monomer I An R1= carbon number consists of an aromatic series functional group of the necessary number. The ether which permits the case where, as for the ionic conduction system monomer II, an R2= carbon number contains the hydrocarbon part of the necessary number, and the hetero atom of the necessary number, Ester, acrylamide, an amide, an alkyl part, and a sulfonic group, It consists of what has the ionic conduction radical in which any one or all of a phosphoric acid carried out the chemical bond to the shape of a straight chain or a branching straight chain. High volume monomer III Two ring compounds surrounded with the silicon or oxygen atom of the necessary number In the cage configuration compound constituted when carrying out silicon-oxygen-silicon association through an oxygen atom in the silicon atoms which face, and connected by silicon-oxygen-silicon association of a necessary number It consists of what has a high functional group. **** which presents the structure in which silicon carried out the chemical bond to the annular aliphatic series system carbon compound of a required-number membered-ring -- A cross linking agent IV consists of an aromatic series ring. These vinyl monomers Copolymerization and the ionic conduction resin which constructed the bridge, a synthetic fiber, or the ceramics, It is characterized by including the fiber aggregate chosen from from among the shape of the shape of the shape of reticulated and textile fabrics which consists of either among glass, a metal, and a nonmetal system element compound, and a nonwoven fabric, and fibril inside the ionic conduction film.

[0010] It is said aromatic series system monomer I further again. t-butyl styrene and the ionic conduction system monomer II are 2-acrylamido-2-methyl propane sulfonic acid and the high volume monomer III. It is

characterized by compound-izing a nonwoven glass fabric in the ionic conduction resin propyl methacrylic POSS and whose cross linking agent IV are bisphenol A glycerate diacrylate.

[0011] The manufacture approach of the above-mentioned ionic conduction film is the aromatic series system monomer I. Weight content 5% – 80%, High volume monomer III The canal polymerization phase by which an organic solvent is further constituted [0.1% – 50% and a cross linking agent IV] for a hydrophobic polymerization initiator from 1% – 85% of each within the limits 0.01% to 20% 0.02% to 30%, The ionic conduction system monomer II 3% – 90%, A hydrophilic polymerization initiator is characterized by sinking in the fiber aggregate in pickup 20%–520% to the vinyl monomer solution which consists of a hydrophilic polymerization phase in which water is contained in 6% – 95% of each range 0.03% to 25% again. In addition, as a hydrophobic polymerization initiator, although azobisisobutyronitril, a benzophenone, benzoyl peroxide, peroxidation t-butyl, etc. are mentioned, it is not limited to these initiators. As a hydrophilic polymerization initiator, although ammonium-peroxydisulfate, potassium-peroxydisulfate, peroxydisulfuric-acid sodium, 2, and 2-azobis [2-(2-imidazoline-2-IRU) propane] dihydrochloride etc. is mentioned, it is not limited to especially these initiators.

[0012] Moreover, other manufacture approaches of the above-mentioned ionic conduction film are the aromatic series system monomers I. Weight content 5% – 80%, High volume monomer III The canal polymerization phase by which an organic solvent is further constituted [0.1% – 50% and a cross linking agent IV] for a hydrophobic polymerization initiator from 1% – 85% of each within the limits 0.01% to 20% 0.02% to 30%, After a hydrophilic polymerization initiator sinks [the ionic conduction system monomer II / water] in the fiber aggregate in pickup 20%–520% 3% to 90% again to the hydrophilic polymerization phase contained in 6% – 95% of each range 0.03% to 25%, It is characterized by making it stick to a fiber aggregate using a synthetic-resin film, irradiating bridge formation energy at a fiber aggregate, and carrying out the polymerization of a vinyl monomer and the cross linking agent.

[0013] The approach of irradiating the fiber aggregate the above-mentioned bridge formation energy A conductor, infrared radiation, Depending on any of far-infrared irradiation equipment they are The ultraviolet radiation or the light exposure machine of the range of the conditions maintained for 0.5 seconds to 4 hours in the range whose vinyl monomer impregnation temperature of a fiber aggregate is 35 degrees C – 220 degrees C, or 190nm – 700nm wavelength is used. A vinyl monomer impregnation body surface 0.5 mW/cm² From to 5600mW/cm² Exposure conditions which become a light-receiving energy range, Or it is characterized by carrying out the bridge formation energy exposure of the electron ray on the conditions irradiated for 0.2 seconds to 5 hours in the range of 20 Mrad-m/min to 360 Mrad-m/min with electron-beam-irradiation equipment.

[0014]

[Embodiment of the Invention] The example of this invention is explained based on a drawing below. About a drawing, the giant-molecule structure of the fluorine system ionic conduction film and drawing 2 drawing 1 The hydrophilic-non-dense aqueous-phase model inside the fluorine system film, The amelioration effectiveness of demand characteristics [in / drawing 3 / the structure of a POSS radical, and drawing 4 , and / in drawing 5 / an example 1], [a methanol expulsive measurement cel] The relation of the weight content of an aromatic series system monomer and an ionic conduction value, [in / in drawing 6 / example 2.] The relation of the weight content of a methanol expulsive radical and film reinforcement, [in / in drawing 7 / an example 3] The relation of the weight content of a cross linking agent and film reinforcement, the relation of the weight content of a polymerization initiator and an ionic conduction value, [in / in drawing 8 / an example 4] [in / in drawing 9 / an example 5] The relation of the weight content of an organic solvent and a methanol expulsive value, [in / in drawing 10 / an example 6] The relation of the polymerization content of an ionic conduction system monomer and an ionic conduction value, [in / in drawing 11 / an example 7] The relation of the weight content of a hydrophilic polymerization initiator and a heat-resistant value, [in / in drawing 12 / an example 8] The relation of the weight content of water and a heat-resistant value, the relation of a pickup and an ionic conduction value, [in / in drawing 13 / an example 9] [in / in drawing 14 / an example 10] The relation of curing temperature and film reinforcement, the relation of the setting time and a methanol abatement value, [in / in drawing 15 / an example 11] [in / in drawing 16 / an example 12] The relation between ultraviolet-visible-ray wavelength [in / in drawing 17 / an example 13], and film reinforcement, the relation of a light-receiving energy density and an ionic conduction value, [in / in drawing 18 / an example 14] The relation of an electron ray reinforcement and a heat-resistant value and drawing 20 show the relation of the light-receiving energy density and ionic conduction value in an example 16. [in / in drawing 19 / an example 15]

[0015] in addition, said aromatic series system monomer I in claim 3 An R1= carbon number consists of an aromatic series functional group to 1–20 pieces. The concrete example of this Styrene, 3-methyl styrene,

4-methyl styrene, t-butyl styrene, sec-butyl styrene, Alpha methyl styrene, trans-beta-methyl styrene, 2-chloro styrene, Although it is 3-chloro styrene, 4-chloro styrene, 2-vinyl naphthalene, 9-vinyl anthracene, a vinyl pyrene, N-vinylcarbazole, 2-vinylpyridine, 4-vinylpyridine, or 1-vinyl imidazole, it is not limited to these. The ether which permits the case where, as for the ionic conduction system monomer II, an R2= carbon number contains the hydrocarbon part to 1-18 pieces, and the hetero atom to 1-5 pieces, Ester, acrylamide, an amide, an alkyl part, and a sulfonic group, It consists of what has the ionic conduction radical in which any one or all of a phosphoric acid carried out the chemical bond to the shape of a straight chain or a branching straight chain. The concrete example of this 2-acrylamido-2-methyl propane sulfonic acid, Although it is 4-styrene sulfonic-acid sodium, sodium allylsulfonate, sodium methallylsulfonate, a vinyl sulfonic acid, a vinyl propane sulfonic acid, ethyl diethyl phosphono acetate, a vinyl phosphoric acid, an allyl compound phosphoric acid, etc. It is not limited to these compounds. High volume monomer III Two ring compounds surrounded with the silicon or oxygen atom to 3-80 pieces In the cage configuration compound constituted when carrying out silicon-oxygen-silicon association through an oxygen atom in the silicon atoms which face, and connected by silicon-oxygen-silicon association of 3-80 It consists of what has a high functional group. **** which presents the structure in which silicon carried out the chemical bond to the annular aliphatic series system carbon compound of three to 12 membered-ring -- For example, although propyl methacrylic POSS, Vinyl POSS, POSS acrylamide, an allyl compound POSS, Metallyl POSS, methacrylic one POSS, acrylic-acid POSS, etc. are mentioned, it is not limited to these compounds. A cross linking agent IV is not limited to these cross linking agents, although it consists of an aromatic series ring and bisphenol A glycerate diacrylate, a divinylbenzene, divinyl naphthalene, diallyl phthalate, diaryl tetrabromo phthalate, a diaryl diphenyl silane, diaryl diphenylphosphine, etc. are mentioned as a concrete example of this. The fiber aggregate chosen from among the shape of the shape of the shape of reticulated [which these vinyl monomers become from either among copolymerization and the ionic conduction resin which constructed the bridge, a synthetic fiber or the ceramics, glass a metal, and a nonmetal system element compound], and textile fabrics, and a nonwoven fabric, and fibril is included inside the ionic conduction film. Although each numerical range of the carbon number of the . above R1 and R2 which is not what is restricted to these compounds although it is silicon carbide, boron carbide, silicon nitride, boron nitride, etc. as a nonmetal system element compound, the silicon of R3 or the oxygen atom number, a silicon-oxygen-silicon joint number, and the number of membered-rings of silicon is desirable range, it is not necessarily limited to each of this numerical range.

[0016]

[Example 1] The ionic conduction film was obtained by dissolving t-butyl styrene 5.25g, 0.8g of 2-acrylamido-2-methyl propane sulfonic acid, propyl methacrylic POSS0.25g, and bisphenol A glycerate diacrylate 1.0g in N and N'-dimethylformamide 8ml and the mixed solvent of 3ml of water, and carrying out heating bridge formation of the solution which added azobisisobutyronitril 20mg and was obtained at 10 degrees C for 3 minutes using a hot calender roll, after sinking into the polypropylene network of 20 meshes at pickup 250%. In addition, the structure of a POSS radical is as being shown in drawing 3.

[0017] The methanol abatement engine performance of the ionic conduction film obtained the account of a top was measured as follows. That is, in the cel configuration for measurement shown in drawing 4, two glass cylinders with doubling cost with a methanol permeability width of face of 10mm (98ml of inner capacity) were prepared, the ionic conduction film with a diameter of 70mm was put between them, the methanol transparency diameter of the ionic conduction film was set to 50mm, 3% of the weight of the methanol water solution was put into the interior of one glass cylinder (methanol phase), and the interior of another glass cylinder was filled up with aqua destillata (aqueous phase). After setting the time of finishing setting up these measurement cels as measurement initiation and sampling water in part from the aqueous phase after 30-minute progress, it analyzed using the Hitachi G-5000 mold gas chromatograph (FID detector), and the quantum of the methanol concentration Mi in the aqueous phase was carried out.

[0018] When considering as the methanol concentration Mf similarly measured using the fluorine system ionic conduction film (example of a comparison), it was defined as the following formula (1) by making a methanol transparency control value into a relative value.

Methanol abatement value = M_f/M_i -- Formula (1)

As the result was shown in drawing 5, compared with the fluorine system ionic conduction film (example of a comparison) used as ionic conduction film of a direct methanol mold fuel cell, the ionic conduction film by this invention showed higher methanol expulsive conventionally.

[0019] About thermal resistance, it evaluated as follows. The part was sampled from said obtained ionic conduction film, and the pyrolysis initiation temperature Ti of the ionic conduction film was measured in air using TG-DTA. The pyrolysis initiation temperature Tf of the conventional fluorine system ionic conduction

film was measured similarly, and the definition was given as a relative value of the value the fluorine system film indicates thermal resistance to be like the following formula (2).

A heat-resistant value = T_i/T_f --- Formula (2)

As the result was shown in drawing 5, the heat-resistant value of the ionic conduction film by this invention was larger than the value of the fluorine system film which is film conventionally, and showed higher thermal resistance.

[0020] About ion conductivity, it evaluated as follows. It stuck on fluororesin plate manufacturing so that *****
1.0cm long, 2.5cm wide, and the platinum foil with a thickness of 10 microns might be prepared in the center section of 4.0cm long, 4.0cm wide, and fluororesin plate manufacturing with a thickness of 0.5cm and the 1.0cm side of the platinum foil might touch 0.5cm long and a 1.0cm wide sump to 1.0cm [about] of the sump of fluororesin plate manufacturing in it.

[0021] After producing these two plates, it dips in 1/40-N nitric-acid water solution of chloroplatinic acid, and they are bath voltage 3.0V and current density 40 mA/cm². Platinum black was plated on the platinum foil for 1 hour. This fluororesin plate manufacturing was dipped into 1% sulfuric acid, the platinum electrode was used for the counter electrode, and each of the fluororesin plate manufacturing of two sheets was followed in the actuation which energizes a platinum-electrode side for 10 minutes in electrical-potential-difference 3.0V by using the platinum-foil side of a negative electrode and fluororesin plate manufacturing as a positive electrode.

[0022] thus, the ionic conduction film cut into 1.0cm long and 1.5cm wide between two fluororesin plate manufacturing of obtained platinum black plating --- inserting --- the platinum foil --- solar TRON company make --- it connected with impedance analyzer S1-1260, and membranous ionic conductivity was computed with the alternating current anodizing process. The ionic conduction value by this invention was defined like the following formula (3).

Ionic conduction value = I_i/I_f --- Formula (3)

If: ionic conductivity I_i : of the conventional fluorine system --- the degree of ionic conduction of the film by this invention --- as the result was shown in drawing 5, also in ion conductivity, it became clear that the ionic conduction film by this invention is conventionally larger than membranous ion conductivity.

[0023] About membranous reinforcement, it evaluated as follows. the stress at the time of pulling 15cm long and the 0.5cm wide ionic conduction film, hanging on a testing machine, and making a sample fracture by hauling in the distance between chucks of 10cm --- the cross section of the ionic conduction film --- ***** --- when setting tensile strength of S_i and the conventional fluorine system film to S_f for tensile strength by things, film reinforcement was defined like a formula (4). film = on the strength --- a S_i/S_f --- type (4) --- as the result was shown in drawing 5, the film reinforcement by this invention had high film reinforcement compared with the conventional fluorine system film.

[0024]

[Example 2] As the result of having measured the ionic conduction value at the time of changing the weight content of t-butyl styrene at the time of preparing the ionic conduction film in an example 1 is shown in drawing 6, in the range whose t-butyl styrene weight content is 5% - 80%, the ionic conduction value is large compared with the film conventionally, and the range indicated to claim 5 is suitable for the weight content of an aromatic series system monomer.

[0025]

[Example 3] Since film reinforcement is conventionally larger than a membranous value in the range whose weight content propyl methacrylic [POSS] is 0.1% - 50% as drawing 7 shows the film reinforcement when changing weight content propyl methacrylic [POSS] in case the ionic conduction film is prepared in an example 1, the range indicated to claim 5 is appropriate to the weight content of a high volume monomer.

[0026]

[Example 4] In case the ionic conduction film is prepared in an example 1, as drawing 8 shows the film change on the strength at the time of changing the weight content of bisphenol A guru cello rate diacrylate as a cross linking agent, it is conventionally larger than a membranous value in 0.02% - 30% of range, and the range indicated to claim 5 is suitable.

[0027]

[Example 5] Since the weight content of a hydrophobic polymerization initiator is larger than the value of the conventional fluorine system film in the range which is 0.01% - 20% as drawing 9 shows the ionic conduction value when changing the weight content of azobisisobutyronitril as a hydrophobic polymerization initiator in an example 1, the range which indicated the weight content of a hydrophobic polymerization initiator to claim 5 is appropriate.

[0028]

[Example 6] When preparing the ionic conduction film in an example 1, as drawing 10 shows the relation between the weight content of an organic solvent, and a methanol abatement value, the methanol abatement value is conventionally larger than a membranous value at the time of 1% – 85% of range, and, as for the weight content of an organic solvent, the range which indicated the weight content of an organic solvent to claim 5 is appropriate.

[0029]

[Example 7] When preparing the ionic conduction film in an example 1, as drawing 11 shows the relation between the weight content of 2-acrylamido-2-methyl propane sulfonic acid, and an ionic conduction value as an ionic conduction system monomer, in the ionic conduction value, the ionic conduction value is conventionally larger than the film at the time of 3% – 90% of range, and, as for the weight content of 2-acrylamido-2-methyl propane sulfonic acid, the range indicated to claim 5 is suitable for the weight content of an ionic conduction system monomer.

[0030]

[Example 8] In case the ionic conduction film is manufactured in an example 1, as the heat-resistant value when changing the weight content of a ** RUOKISONI ammonium sulfate as a hydrophilic polymerization initiator is shown in drawing 12, in the heat-resistant value, the weight content of a ** RUOKISONI ammonium sulfate is larger than the value of the conventional fluorine system film at 0.03% – 25% of within the limits, and the range indicated to claim 5 is suitable for the weight content of a hydrophilic polymerization initiator.

[0031]

[Example 9] In case the ionic conduction film is manufactured in an example 1, as drawing 13 shows the heat-resistant value when changing the weight content of water, thermal resistance is conventionally larger than the film in 6% – 95% of range, and, as for the weight content of water, the range indicated to claim 5 is suitable for the weight content of water.

[0032]

[Example 10] When manufacturing the ionic conduction film in an example 1, in case the polypropylene network which is the fiber aggregate is sunk into a monomer solution phase, as the relation between pickup and an ionic conduction value is shown in drawing 14, the range where pickup indicated the pickup of the fiber aggregate to claim 5 by the ionic conduction value being conventionally larger than the film in 20% – 520% of range is appropriate.

[0033]

[Example 11] When making it harden according to the fiber aggregate and bridge formation which sank in the vinyl monomer solution in the example 1, as drawing 15 shows the reinforcement of the ionic conduction film when changing curing temperature, curing temperature is conventionally larger than a membranous value in 35 degrees C – 220 degrees C, and the range indicated to claim 7 is suitable for curing temperature.

[0034]

[Example 12] As the methanol abatement value which the ionic conduction film when changing the setting time of the ionic conduction film in an example 1 shows is shown in drawing 16, the setting time is conventionally larger than membranous physical properties in the range of 0.5 seconds – 4 hours, and the range indicated to claim 7 is suitable for the setting time.

[0035]

[Example 13] When the content of combination which changed the azobisisobutyronitril of a hydrophobic polymerization initiator to the benzophenone is adopted among the monomer solution in an example 1 and a black light is used instead of a hot calender roll, about film reinforcement, as shown in drawing 17, the wavelength of ultraviolet rays is conventionally larger than a membranous value in the range which is 190nm – 700nm, and the range indicated to claim 7 is suitable for the wavelength of the ultraviolet rays by the black light.

[0036]

[Example 14] when changing the light-receiving energy density of the ultraviolet-visible ray which a vinyl monomer impregnation body surface receives in an example 13, the ionic conduction value change of the ionic conduction film is shown in drawing 18 — as — a light-receiving energy density — 0.5 mW/cm² from — 5600 mW/cm² Membranous ion conductivity is conventionally excelled in the range, and the range which indicated the light-receiving energy density to claim 7 is suitable.

[0037]

[Example 15] Since the thermal resistance which the ionic conduction film shows became conventionally larger than the film when the heat-resistant value of the ionic conduction film when changing the exposure

energy of the electron ray at the time of using electron-beam-irradiation equipment instead of an ultraviolet ray lamp in an example 13 irradiated an electron ray in the range of 20 Mrad-m/min - 30 Mrad-m/min, as shown in drawing 19, the range which indicated the exposure energy of the electron ray by electron-beam-irradiation equipment to claim 7 is suitable.

[0038]

[Example 16] The ionic conduction value of the ionic conduction film when changing the irradiation time of an electron ray in an example 15 has exceeded the membranous value conventionally in 0.2 seconds - 5 hours, as shown in drawing 20, and the range indicated to claim 7 is suitable for the irradiation time of the electron ray by electron-beam-irradiation equipment.

[0039] By the way, in a direct methanol mold fuel cell (DMFC), a methanol crossover is an important problem. It is said that a methanol checks electrode catalytic reaction by permeating the inside of the ionic conduction film from an anode (a negative electrode, fuel electrode), and permeating a cathode (a positive electrode, oxygen pole) with moisture. The main electrode reaction in DMFC is as follows.

anode: $\text{CH}_3\text{OH} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 6\text{H}^+ + 6\text{e}^-$ cathode: $\frac{1}{2}\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{O}$, among these the methanol which has permeated check the reduction reaction of a cathode, the output as the whole DMFC, i.e., the generation efficiency of a cell, will decline.

[0040] Then, this invention controlled diffusion of the methanol in the film by introducing a methanol expulsive functional group into the macromolecule structure which forms the ionic conduction film. As shown in drawing 3, the POSS radical which is heptacyclo pentyl PENTASHIKUROOKUTA siloxane 1-IRU as a methanol expulsive functional group was introduced. The structure of drawing 3 has the form in which two annular silicates carried out the chemical bond (Si-O-Si). The methanol molecule which diffuses the inside of the film takes some moisture with it, and forms the methanol water molecule ensemble. Since said POSS radical is having cage configuration structure, these methanols water molecule ensemble is incorporated in a cage.

[0041] Next, silicon belongs to the category with high hydrophobicity and an atomic radius quite small in about 0.04nm and an element, and also has high hydrophobicity (oleophilic), and hydrophobicity has localized it. Hydrophobicity is large although methanol molecules are very few [the part of a methyl group] differences than water. Then, since the methanol water molecule incorporated in said cage is attracted by the hydrophobic-hydrophobic interaction, delay arises at the rate which escapes from a POSS radical rather than a water molecule. Consequently, the diffusion in the film is controlled by the cage effect and the hydrophobic localization effectiveness that a POSS radical has a methanol molecule. In addition, a POSS radical can raise the hydrophobicity in the film, without raising the hydrophobicity of the whole ionic conduction film, since hydrophobicity is carrying out localization.

[0042] About the design of the polymer molecule for using for the ionic conduction film of DMFC, in the fluorine system film used for conventional PEFC and conventional DMFC, compatibility of a fluorine with a methanol is fundamentally large, and the effectiveness which controls a crossover can seldom be expected. Therefore, the raw material (monomer) of a hydrocarbon system was used in the molecular design of these polymers.

[0043] t-butyl styrene was chosen as indicated to claim 4 as an example of the structural material. This t-butyl styrene has the more large hydrophobicity of a monomer. Therefore, since a larger hydrophobic-hydrophobic interaction is expectable, membrane structure can be strengthened more. Moreover, the biphenol A type was used for the cross linking agent. The structure of this cross linking agent has bonding strength high in a polymer generally. Therefore, bridge formation reinforcement and thermal resistance are held by these.

[0044] In addition, the ionic conduction film by this invention can be applied to the flat panel of an electrochemistry type sensor, a light emitting device, and a laptop computer etc. other than a polymer electrolyte fuel cell.

[Translation done.]

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] Macromolecule structural drawing of this invention fluorine system ionic conduction film

[Drawing 2] The hydrophilic-non-dense aqueous-phase model inside the fluorine system film in this invention

[Drawing 3] Structural drawing of the POSS radical in this invention

[Drawing 4] Drawing showing the methanol expulsive measurement cel used in this invention

[Drawing 5] The bar graph which shows the amelioration effectiveness of the demand characteristics in the example 1 of this invention

[Drawing 6] The graph which shows the relation of the weight content of an aromatic series system monomer and the ionic conduction value in the example 2 of this invention

[Drawing 7] The graph which shows the relation of the weight content of a methanol expulsive radical and film reinforcement in the example 3 of this invention

[Drawing 8] The graph which shows the relation of the weight content of a cross linking agent and film reinforcement in the example 4 of this invention

[Drawing 9] The graph which shows the relation of the weight content of a polymerization initiator and the ionic conduction film value in the example 5 of this invention

[Drawing 10] The related **** graph of the weight content of an organic solvent and the methanol expulsive value in the example 6 of this invention

[Drawing 11] The graph which shows the relation of the polymerization content of an ionic conduction system monomer and the ionic conduction value in an example 7

[Drawing 12] The graph which shows the relation of the weight content of a hydrophilic polymerization initiator and the heat-resistant value in an example 8

[Drawing 13] The graph which shows the relation of the weight content of water and the heat-resistant value in the example 9 of this invention

[Drawing 14] The graph which shows the relation of the pickup and ionic conduction value in the example 10 of this invention

[Drawing 15] The graph which shows the relation of the curing temperature and film reinforcement in the example 11 of this invention

[Drawing 16] The graph which shows the relation of the setting time and the methanol abatement value in the example 12 of this invention

[Drawing 17] The graph which shows the relation between the ultraviolet-visible-ray wavelength in the example 13 of this invention, and film reinforcement

[Drawing 18] The graph which shows the relation of the light-receiving energy density and ionic conduction value in the example 14 of this invention

[Drawing 19] The graph which shows the relation of the electron ray reinforcement and the heat-resistant value in the example 15 of this invention

[Drawing 20] The graph which shows the relation of the electron-beam-irradiation time amount and the ionic conduction value in the example 16 of this invention

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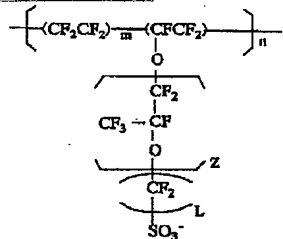
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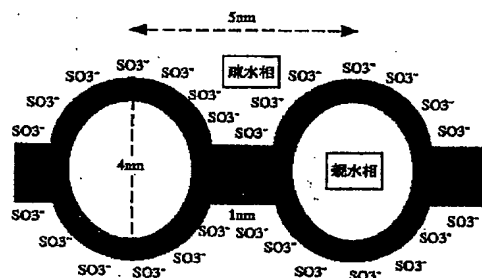
DRAWINGS

[Drawing 1]

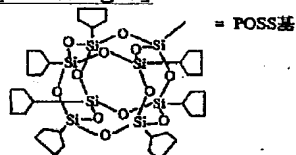


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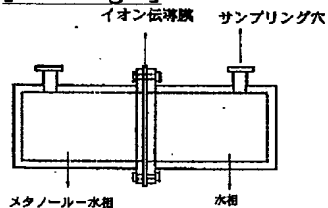
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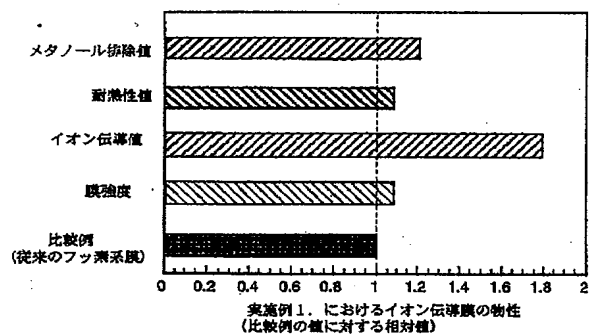
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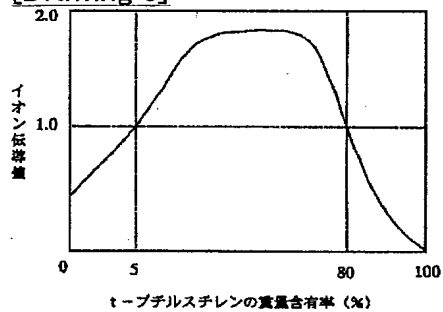
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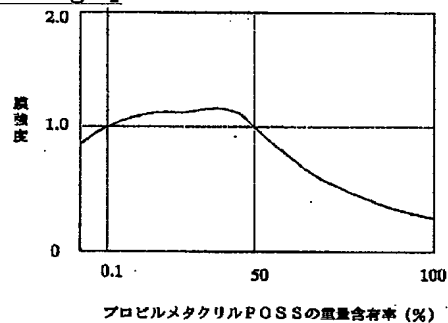
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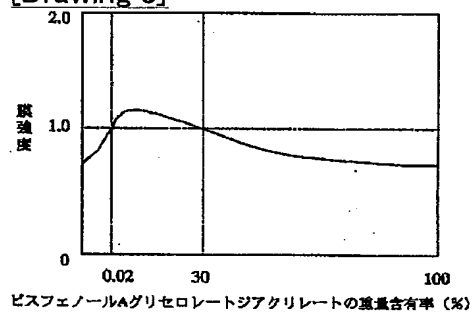
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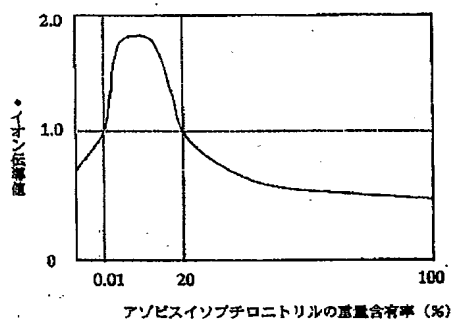
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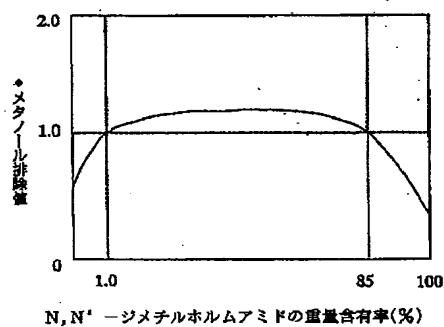
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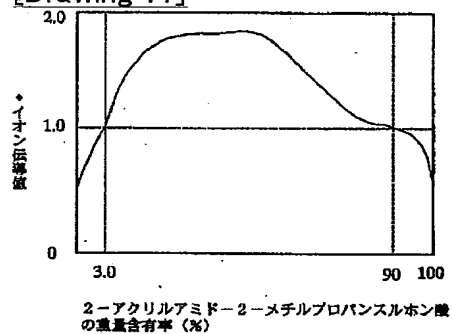
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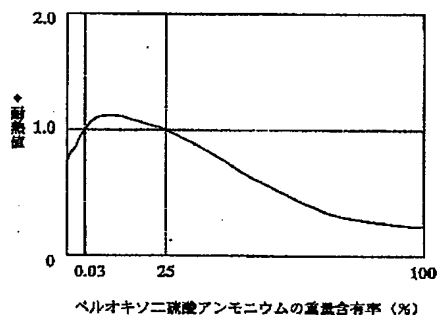
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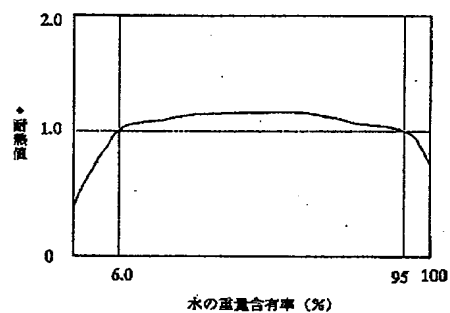
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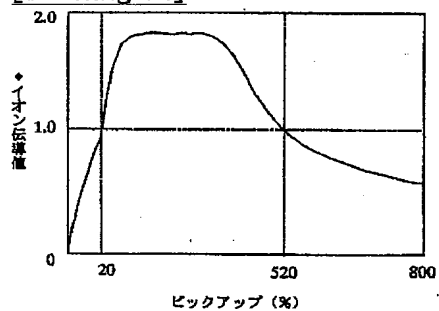
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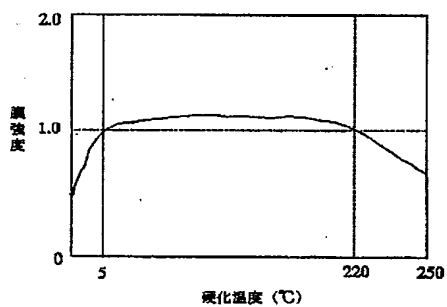
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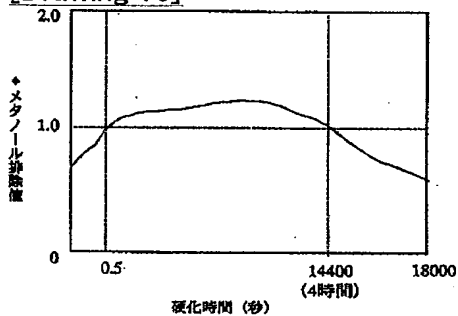
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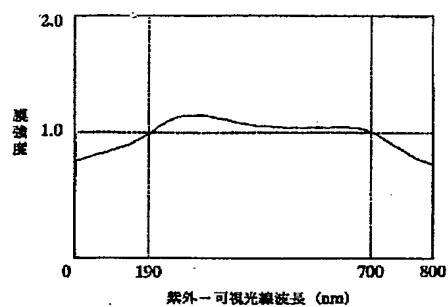
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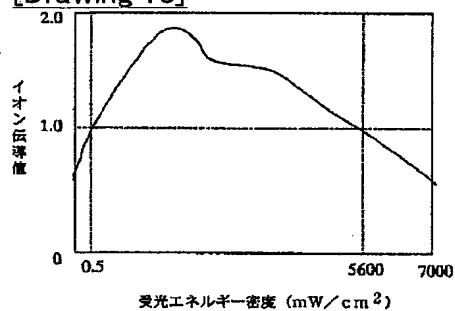
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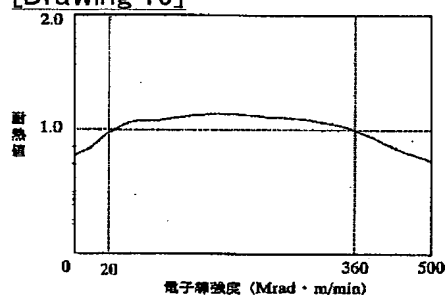
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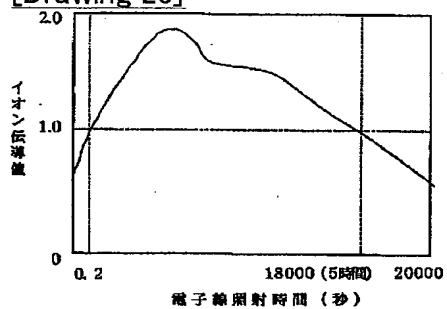
[Drawing 18]



[Drawing 19]



[Drawing 20]



[Translation done.]

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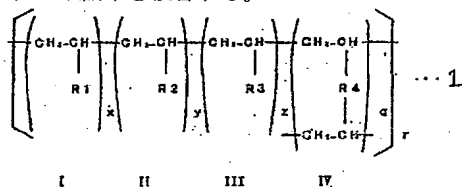
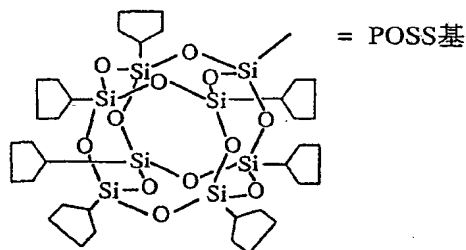
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(54) 【発明の名称】 イオン伝導膜及びその製造方法

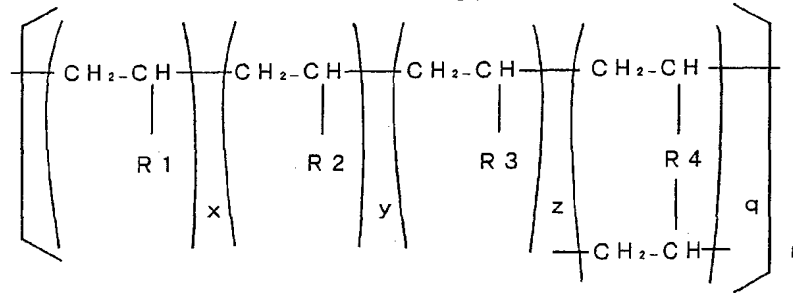
(57) 【要約】 (修正有)

【課題】メタノールバリア性、耐熱性、高いイオン伝導性、力学的強度及び低価格性を有する固体高分子燃料電池用イオン伝導膜とその製造方法の提供。

【解決手段】芳香族系モノマーI、イオン伝導性モノマーII、高容積モノマーIII、架橋剤IVからなる式1のイオン伝導性樹脂と繊維集合体とを膜状に複合する。例えば、Iとして α -ブチルスチレン、IIとして2-アクリルアミド-2-メチルプロパンスルホン酸、IIIとしてプロピルメタクリルPOSS、IVとしてビスフェノールAグリセロレートジアクリレートを用いたイオン伝導樹脂中にガラス不織布を複合する。



【特許請求の範囲】



I

II

III

IV

芳香族系モノマーI、イオン伝導系モノマーII、高容積モノマーIII及び架橋剤IVからなる上記構造式1のイオン伝導樹脂と繊維集合体とを膜状に複合したことを特徴とするイオン伝導膜。

【請求項2】芳香族系モノマーIが芳香族系ビニルモノマーからなり、イオン伝導系モノマーIIが酸性基を有するビニルモノマーからなり、高容積モノマーIIIがケイ素-酸素、ケイ素-炭素、炭素-炭素結合の何れか1つ又は全部により立体的で籠形状を形成したものからなり、架橋剤IVは芳香族環からなり、有機繊維又は無機繊維の網状、織布状、不織布状、フィブリル状のうちから選択された繊維集合体と複合化されたことを特徴とする請求項1に記載のイオン伝導膜。

【請求項3】芳香族系モノマーIはR1＝炭素数が所要個数の芳香族官能基からなり、イオン伝導系モノマーIIはR2＝炭素数が所要個数の炭化水素部分と所要個数のヘテロ原子を含む場合を許容するエーテル、エステル、アクリルアミド、アミド、アルキル部分及びスルホン酸基、リン酸の何れか1つ又は全部とが直鎖又は分岐直鎖状に化学結合したイオン伝導基を有するものからなり、高容積モノマーIIIは所要個数のケイ素又は酸素原子によって囲まれる複数個の環状化合物が、相対するケイ素原子同士において酸素原子を介してケイ素-酸素-ケイ素結合する場合、所要本数のケイ素-酸素-ケイ素結合によって連結されることにより構成する籠形状化合物において、ケイ素が所要数員環の環状脂肪族炭素化合物と化学結合した構造を呈する嵩さ高い官能基を有するものからなり、架橋剤IVは芳香族環からなり、これらのビニルモノマーが共重合及び架橋したイオン伝導樹脂と合成繊維又はセラミックス、ガラス、金属、非金属系元素化合物のうち何れかからなる網状、織布状、不織布状、フィブリル状のうちから選択された繊維集合体がイオン伝導膜内部に包含されたことを特徴とする請求項1に記載のイオン伝導膜。

【請求項4】芳香族系モノマーIが α -ブチルスチレン、イオン伝導系モノマーIIが2-アクリルアミド-2-メチルプロパンスルホン酸、高容積モノマーIIIがプロピルメタクリルPOSS、架橋剤IVがビスフェノールA

グリセロールジアクリレートであるイオン伝導樹脂中にガラス不織布が複合化されたことを特徴とする請求項1に記載のイオン伝導膜。

【請求項5】請求項1～4何れかに記載のイオン伝導膜を製造する際に、芳香族系モノマーIの重量含有率が5%～80%、高容積モノマーIIIが0.1%～50%、また、架橋剤IVが0.02%～30%、疎水性重合開始剤が0.01%～20%さらには有機溶剤が1%～85%の各範囲内で構成される疎水重合相と、イオン伝導系モノマーIIが3%～90%、親水性重合開始剤が0.03%～25%また水が6%～95%の各範囲で含まれる親水性重合相からなるビニルモノマー溶液に対して繊維集合体をピックアップ20%～520%の範囲で含浸したことを特徴とするイオン伝導膜の製造方法。

【請求項6】請求項1～4何れかに記載のイオン伝導膜を製造する際に、芳香族系モノマーIの重量含有率が5%～80%、高容積モノマーIIIが0.1%～50%、また、架橋剤IVが0.02%～30%、疎水性重合開始剤が0.01%～20%さらには有機溶剤が1%～85%の各範囲内で構成される疎水重合相と、イオン伝導系モノマーIIが3%～90%、親水性重合開始剤が0.03%～25%また水が6%～95%の各範囲で含まれる親水性重合相に対して繊維集合体をピックアップ20%～520%の範囲で含浸した後、合成樹脂フィルムを用いて繊維集合体に密着させ、架橋エネルギーを繊維集合体に照射してビニルモノマー及び架橋剤を重合させることを特徴とするイオン伝導膜の製造方法。

【請求項7】熱伝導体、赤外線、遠赤外線照射装置の何れかにより繊維集合体のビニルモノマー含浸温度が35℃～220℃の範囲で0.5秒～4時間維持される条件又は波長190nm～700nmの範囲の紫外光又は可視光照射器を用いてビニルモノマー含浸体表面が0.5mW/cm²から5600mW/cm²の受光エネルギー範囲になるような照射条件、あるいは電子線照射装置によって20Mrad・m/minから360Mrad・m/minの範囲で電子線を0.2秒～5時間照射する条件で架橋エネルギー照射することを特徴とする請求項6に記載のイオン伝導膜の製造方法。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、高いイオン伝導性と耐熱性及びメタノールバリア性を有するイオン伝導膜及びその製造方法に関するものである。

【0002】

【従来の技術】大気汚染や地球温暖化などの問題解決への取り組みが叫ばれている中、排気ガス抑制型自動車の開発に対する期待が高まりを見せている。特に固体高分子型燃料電池は、エネルギー総合効率が高く、環境性が高いなどの様々な利点があり、新しいクリーンな電気自動車用発電形式として期待が大きい。一般的に燃料電池と呼ばれる発電方式は、水の電気分解の逆反応を利用して燃料（水素など）の持っているエネルギーを直接電気エネルギーとして取り出すものである。一般に構成上の特徴からリン酸型、溶融炭酸塩型、固体電解質型及び固体高分子型の4種類に代表される。

【0003】前記4種類に代表される中の固体高分子型燃料電池（PEFC）に用いられているイオン伝導膜としては、商品名「ナフィオン」などのパーフルオロアルキルスルホン酸の非架橋型のイオン伝導膜が用いられてきた。

【0004】

【発明が解決しようとする課題】上記フッ素系イオン伝導膜は高い化学的安定性と耐熱性を有しており、固体高分子型燃料電池の実用性を高めるために重要な役割を果たしている。しかしながら、従来用いられているフッ素系イオン伝導膜は、本来食塩を電気分解して苛性ソーダと塩素ガスを工業レベルで取り出す際の隔膜として開発

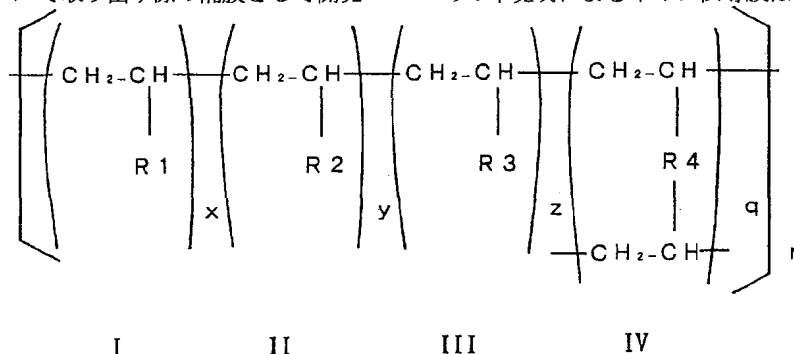
されたものであって、燃料電池用の材料として開発されたものではなく、膜抵抗が大きいことから燃料電池の発電エネルギー効率が低下していることが指摘されており、多くの改良点が課題として残されている。

【0005】また、ダイレクトメタノール型燃料電池（DMFC）の基礎研究の分野においてもフッ素系イオン伝導膜が有する多数の優位性を模倣しながら補足的にダイレクトメタノール型燃料電池として必要な機能を加えて行く方法が採用される場合が多い。これらの機能としては、1）メタノールバリア性、2）耐熱性、3）イオン伝導性、4）力学的強度、5）低価格性などであるが、これらの機能は全て関連しており、これらの中で1つの機能を向上させて行くと他の機能が低下する傾向が有る。例えば、ダイレクトメタノール型燃料電池の場合は現状では触媒活性が低いことから電池の稼動温度を130℃～200℃まで高い温度範囲に設定しなければならない。しかしながら、従来膜においてはスルホン酸基が有する高い酸性の影響によりポリマー主鎖の切断が発生するなどの酸化分解が起こる。さらに、メタノールクロスオーバーに起因したカソードにおける還元反応の妨害が起こり、電池の発電効率が低下する。従って、上記の機能をバランスよく向上させることが課題である。

【0006】本発明の目的は上記の課題に鑑みて、メタノールバリア性、耐熱性、高いイオン伝導性、力学的強度及び低価格性を有するイオン伝導膜及びその製造方法を提供することである。

【0007】

【課題を解決するための手段】上記の目的を達成するための本発明によるイオン伝導膜は、（構造式1）



芳香族系モノマーI、イオン伝導系モノマーII、高容積モノマーIII及び架橋剤IVからなる上記構造式1のイオン伝導樹脂と繊維集合体とを膜状に複合したことを特徴とするものである。

【0008】また、前記の芳香族系モノマーIが芳香族系ビニルモノマーからなり、イオン伝導系モノマーIIが酸性基を有するビニルモノマーからなり、高容積モノマーIIIがケイ素-酸素、ケイ素-炭素、炭素-炭素結合の何れか1つ又は全部により立体的で籠形状を形成したものからなり、架橋剤IVは芳香族環からなり、有機繊維

又は無機繊維の網状、織布状、不織布状、フィブリル状のうちから選択された繊維集合体と複合化されたことを特徴とするものである。

【0009】さらに、前記の芳香族系モノマーIはR1＝炭素数が所要個数の芳香族官能基からなり、イオン伝導系モノマーIIはR2＝炭素数が所要個数の炭化水素部分と所要個数のヘテロ原子を含む場合を許容するエーテル、エステル、アクリルアミド、アミド、アルキル部分及びスルホン酸基、リン酸の何れか1つ又は全部とが直鎖又は分岐直鎖状に化学結合したイオン伝導基を有する

ものからなり、高容積モノマーIIIは所要個数のケイ素又は酸素原子によって囲まれる2個の環状化合物が、相対するケイ素原子同士において酸素原子を介してケイ素-酸素-ケイ素結合する場合、所要本数のケイ素-酸素-ケイ素結合によって連結されることにより構成する籠形状化合物において、ケイ素が所要数員環の環状脂肪族系炭素化合物と化学結合した構造を呈する嵩さ高い官能基を有するものからなり、架橋剤IVは芳香族環からなり、これらのビニルモノマーが共重合及び架橋したイオン伝導樹脂と合成繊維又はセラミックス、ガラス、金属、非金属系元素化合物のうち何れかからなる網状、繊維状、不繊維状、フィブリル状のうちから選択された繊維集合体がイオン伝導膜内部に包含されたことを特徴とするものである。

【0010】さらにまた、前記芳香族系モノマーIが α -ブチルスチレン、イオン伝導系モノマーIIが2-アクリルアミド-2-メチルプロパンスルホン酸、高容積モノマーIIIがプロピルメタクリルPOSS、架橋剤IVがビスフェノールAグリセレートジアクリレートであるイオン伝導樹脂中にガラス不織布が複合化されたことを特徴とするものである。

【0011】上記イオン伝導膜の製造方法は芳香族系モノマーIの重量含有率が5%~80%、高容積モノマーIIIが0.1%~50%、また架橋剤IVが0.02%~30%、疎水性重合開始剤が0.01%~20%さらには有機溶剤が1%~85%の各範囲内で構成される疎水重合相と、イオン伝導系モノマーIIが3%~90%、親水性重合開始剤が0.03%~25%また水が6%~95%の各範囲で含まれる親水性重合相からなるビニルモノマー溶液に対して繊維集合体をピックアップ20%~520%の範囲で含浸したことを特徴とするものである。尚、疎水性重合開始剤としては、アゾビスイソブチロニトリル、ベンゾフェノン、ベンゾイルパーオキサイド、過酸化 α -ブチルなどが挙げられるが、これらの開始剤に限定されるものではない。親水性重合開始剤としては、ペルオキシ二硫酸アンモニウム、ペルオキシ二硫酸カリウム、ペルオキシ二硫酸ナトリウム、2,2-アゾビス[2-(2-イミダゾリナー2-イル)プロパン]二塩酸塩などが挙げられるが、特にこれら開始剤に

限定されるものではない。

【0012】また、上記イオン伝導膜の他の製造方法は、芳香族系モノマーIの重量含有率が5%~80%、高容積モノマーIIIが0.1%~50%、また架橋剤IVが0.02%~30%、疎水性重合開始剤が0.01%~20%さらには有機溶剤が1%~85%の各範囲内で構成される疎水重合相と、イオン伝導系モノマーIIが3%~90%、親水性重合開始剤が0.03%~25%また水が6%~95%の各範囲で含まれる親水性重合相に対して繊維集合体をピックアップ20%~520%の範囲で含浸した後、合成樹脂フィルムを用いて繊維集合体

に密着させ、架橋エネルギーを繊維集合体に照射してビニルモノマー及び架橋剤を重合させることを特徴とするものである。

【0013】上記架橋エネルギーを繊維集合体に照射する方法は、熱伝導体、赤外線、遠赤外線照射装置の何れかにより繊維集合体のビニルモノマー含浸温度が35℃~220℃の範囲で0.5秒~4時間維持される条件又は波長190nm~700nmの範囲の紫外光又は可視光照射器を用いてビニルモノマー含浸体表面が0.5mW/cm²から5600mW/cm²の受光エネルギー範囲になるような照射条件、あるいは電子線照射装置によって20Mrad・m/minから360Mrad・m/minの範囲で電子線を0.2秒~5時間照射する条件で架橋エネルギー照射することを特徴とするものである。

【0014】

【発明の実施の形態】以下本発明の実施例を図面に基いて説明する。図面について、図1はフッ素系イオン伝導膜の高分子構造、図2はフッ素系膜内部の親水-疎水相モデル、図3はPOSS基の構造、図4はメタノール排除性測定セル、図5は実施例1における要求特性の改良効果、図6は実施例2における芳香族系モノマーの重量含有率とイオン伝導値との関係、図7は実施例3におけるメタノール排除性基の重量含有率と膜強度との関係、図8は実施例4における架橋剤の重量含有率と膜強度との関係、図9は実施例5における重合開始剤の重量含有率とイオン伝導値との関係、図10は実施例6における有機溶剤の重量含有率とメタノール排除性値との関係、図11は実施例7におけるイオン伝導系モノマーの重合含有率とイオン伝導値との関係、図12は実施例8における親水性重合開始剤の重量含有率と耐熱値との関係、図13は実施例9における水の重量含有率と耐熱値との関係、図14は実施例10におけるピックアップとイオン伝導値との関係、図15は実施例11における硬化温度と膜強度との関係、図16は実施例12における硬化時間とメタノール排除値との関係、図17は実施例13における紫外-可視光線波長と膜強度の関係、図18は実施例14における受光エネルギー密度とイオン伝導値との関係、図19は実施例15における電子線強度と耐熱値との関係、図20は実施例16における受光エネルギー密度とイオン伝導値との関係を示すものである。

【0015】尚、請求項3における前記芳香族系モノマーIは、R1=炭素数が1~20個までの芳香族官能基からなり、これの具体的な例はスチレン、3-メチルスチレン、4-メチルスチレン、 α -ブチルスチレン、sec-ブチルスチレン、 α -メチルスチレン、trans- β -メチルスチレン、2-クロロスチレン、3-クロロスチレン、4-クロロスチレン、2-ビニルナフタレン、9-ビニルアントラセン、ビニルピレン、N-ビ

ニルカルバゾール、2-ビニルピリジン、4-ビニルピリジン、或いは1-ビニルイミダゾールなどであるが、これらに限定されるものではない。イオン伝導系モノマーIIはR2=炭素数が1~18個までの炭化水素部分と1~5個までのヘテロ原子を含む場合を許容するエーテル、エステル、アクリルアミド、アミド、アルキル部分及びスルホン酸基、リン酸の何れか1つ又は全部が直鎖又は分岐直鎖状に化学結合したイオン伝導基を有するものからなり、これの具体的な例は2-アクリルアミド-2-メチルプロパンスルホン酸、4-スチレンスルホン酸ナトリウム、アリルスルホン酸ナトリウム、メタリルスルホン酸ナトリウム、ビニルスルホン酸、ビニルプロパンスルホン酸、エチルジエチルホスホアセテート、ビニリン酸、アリリン酸などであるが、これらの化合物に限定されるものではない。高容積モノマーIIIは3~80個までのケイ素又は酸素原子によって囲まれる2個の環状化合物が、相対するケイ素原子同士において酸素原子を介してケイ素-酸素-ケイ素結合する場合、3~80本のケイ素-酸素-ケイ素結合によって連結されることにより構成する籠形状化合物において、ケイ素が3~12員環の環状脂肪族系炭素化合物と化学結合した構造を呈する高さ高い官能基を有するものからなり、例えばプロピルメタクリルPOSS、ビニルPOSS、POSSアクリルアミド、アリルPOSS、メタリルPOSS、メタクリルPOSS、アクリル酸POSS等が挙げられるが、これらの化合物に限定されるものではない。架橋剤IVは芳香族環からなり、これの具体的な例としてはビスフェノールAグリセロレートジアクリレート、ジビニルベンゼン、ジビニルナフタレン、ジアリルフタレート、ジアリルテトラプロモフタレート、ジアリルジフェニルシラン、ジアリルジフェニルホスフィン等が挙げられるが、これらの架橋剤に限定されるものではない。これらのビニルモノマーが共重合及び架橋したイオン伝導樹脂と合成繊維又はセラミックス、ガラス、金属、非金属系元素化合物のうち何れかからなる網状、織布状、不織布状、フィブリル状のうちから選択された繊維集合体がイオン伝導膜内部に包含されたものである。非金属系元素化合物としては炭化ケイ素、炭化ホウ素、窒化ケイ素、窒化ホウ素などであるが、これらの化合物に限られるものではない。上記R1、R2の炭素数、R3のケイ素又は酸素原子個数、ケイ素-酸素-ケイ素結合本数及びケイ素の員環数の各数値範囲が望ましい範囲であるが、必ずしもこの各数値範囲に限定されるものではない。

【0016】

【実施例1】 t-ブチルスチレン5.25g、2-アクリルアミド-2-メチルプロパンスルホン酸0.8g、プロピルメタクリルPOSS0.25g、ビスフェノールAグリセロレートジアクリレート1.0gをN、N'-ジメチルホルムアミド8ml及び水3mlの混合溶媒に

溶解させ、アゾビスイソブチロニトリル20mgを添加して得られた溶液を20メッシュのポリプロピレンネットにピックアップ250%で含浸した後、熱ロールを用いて10℃で3分加熱架橋することにより、イオン伝導膜を得た。尚、POSS基の構造は図3に示す通りである。

【0017】上記得られたイオン伝導膜のメタノール排除性能を次のようにして測定した。すなわち図4に示す測定用セル構成において、メタノール透過性幅10mmの合わせ代付きガラス円筒(内容量98ml)2個を準備し、その間に直径70mmのイオン伝導膜を挟み込んで、イオン伝導膜のメタノール透過直径を50mmとし、一方のガラス円筒内部には3重量%のメタノール水溶液をいれ(メタノール相)、もう一方のガラス円筒内部には蒸留水を充填した(水相)。これらの測定セルを組み上げた時を測定開始と定め、30分経過後の水相から一部水をサンプリングした後、日立製作所G-5000型ガスクロマトグラフ(FID検出器)を用いて分析し水相中のメタノール濃度Miを定量した。

【0018】同様にしてフッ素系イオン伝導膜(比較例)を用いて測定したメタノール濃度Mfとすると、メタノール透過抑制値を相対値として下記の式(1)のように定義した。

$$\text{メタノール排除値} = Mf / Mi \cdots \text{式(1)}$$

その結果は図5に示すように、従来、直接メタノール型燃料電池のイオン伝導膜として用いられているフッ素系イオン伝導膜(比較例)に比べて本発明によるイオン伝導膜は、より高いメタノール排除性を示した。

【0019】耐熱性に関しては、次のようにして評価した。前記得られたイオン伝導膜から一部をサンプリングし、TG-DTAを用いて空気中にてイオン伝導膜の熱分解開始温度Tiを測定した。同様にして従来のフッ素系イオン伝導膜の熱分解開始温度Tfを測定し、下記の式(2)のように耐熱性をフッ素系膜が示す値の相対値として定義した。

$$\text{耐熱性値} = Ti / Tf \cdots \text{式(2)}$$

その結果は図5に示すように、本発明によるイオン伝導膜の耐熱性値は従来膜であるフッ素系膜の値より大きく、より高い耐熱性を示した。

【0020】イオン伝導性に関しては次のようにして評価した。縦4.0cm、横4.0cm、厚み0.5cmのフッ素樹脂製板の中央部に縦0.5cm、横1.0cmの液だめを削り貫いて、縦1.0cm、横2.5cm、厚み10ミクロンの白金箔を調製し、白金箔の1.0cmの辺が、フッ素樹脂製板の液だめの1.0cm辺に対して接するようにフッ素樹脂製板上に貼付した。

【0021】この板を2個作製した後に、塩化白金酸の1/40N硝酸水溶液に浸し、浴電圧3.0V、電流密度40mA/cm²にて1時間、白金箔上に白金黒をメッキした。このフッ素樹脂製板を1%硫酸中に浸して

対極に白金電極を用いて、白金電極側を負極、フッ素樹脂製板の白金箔側を正極として電圧 3.0V にて 10 分間通電する操作を 2 枚のフッ素樹脂製板のそれぞれについて行った。

【0022】このようにして得られた白金黒メッキのフッ素樹脂製板 2 枚の間に縦 1.0cm、横 1.5cm にカットしたイオン伝導膜を挟み込み、白金箔をソーラートロン社製インピーダンスアナライザ S1-1260 に接続し、交流法により膜のイオン伝導度を算出した。本発明によるイオン伝導値を下記の式 (3) のように定義した。

イオン伝導値 = I_i / I_f … 式 (3)

I_f : 従来のフッ素系のイオン伝導度

I_i : 本発明による膜のイオン伝導度

その結果は図 5 に示すように、イオン伝導性においても本発明によるイオン伝導膜の方が従来膜のイオン伝導性よりも大きいことが判明した。

【0023】膜の強度に関しては、次のようにして評価した。縦 15cm、横 0.5cm のイオン伝導膜を引っ張り試験機に掛け、チャック間距離 10cm にてサンプルを引っ張りにより破断させたときの応力をイオン伝導膜の断面積で除すことによって引っ張り強度を S_i 、従来のフッ素系膜の引っ張り強度を S_f とするとき、膜強度を式 (4) のように定義した。膜強度 = S_i / S_f … 式 (4) その結果は図 5 に示すように、本発明による膜強度は従来のフッ素系膜に比べて高い膜強度を有していた。

【0024】

【実施例 2】実施例 1 においてイオン伝導膜を調製する際の t -ブチルスチレンの重量含有率を変化させた場合のイオン伝導値を測定した結果は図 6 に示すように、 t -ブチルスチレン重量含有率が 5%~80% の範囲においてイオン伝導値が従来膜に比べて大きくなっており、芳香族系モノマーの重量含有率は請求項 5 に記載した範囲が適切である。

【0025】

【実施例 3】実施例 1 においてイオン伝導膜を調製する際に、プロピルメタクリル POSS の重量含有率を変化させたときの膜強度は図 7 で示すように、プロピルメタクリル POSS の重量含有率が 0.1%~50% の範囲において膜強度が従来膜の値よりも大きくなっていることから、高容積モノマーの重量含有率は請求項 5 に記載した範囲が妥当である。

【0026】

【実施例 4】実施例 1 においてイオン伝導膜を調製する際に、架橋剤としてビスフェノール A グルセレートジアクリレート の重量含有率を変化させた場合の膜強度変化は図 8 で示すように、0.02%~30% の範囲で従来膜の値よりも大きくなっており、請求項 5 に記載した範囲が適切である。

【0027】

【実施例 5】実施例 1 において疎水性重合開始剤としてアゾビスイソブチロニトリルの重量含有率を変化させたときのイオン伝導値は図 9 で示すように、疎水性重合開始剤の重量含有率が 0.01%~20% の範囲において従来のフッ素系膜の値より大きくなっていることから、疎水性重合開始剤の重量含有率は請求項 5 に記載した範囲は妥当である。

【0028】

【実施例 6】実施例 1 においてイオン伝導膜を調製する場合、有機溶剤の重量含有率とメタノール排除値との関係は、図 10 で示すように、有機溶剤の重量含有率は 1%~85% の範囲のときにメタノール排除値が従来膜の値よりも大きくなっており、有機溶剤の重量含有率は請求項 5 に記載した範囲は妥当である。

【0029】

【実施例 7】実施例 1 においてイオン伝導膜を調製する場合にイオン伝導系モノマーとして 2-アクリルアミド-2-メチルプロパンスルホン酸の重量含有率とイオン伝導値との関係は図 11 で示すように、イオン伝導値は 2-アクリルアミド-2-メチルプロパンスルホン酸の重量含有率は 3%~90% の範囲のときにイオン伝導値が従来膜よりも大きくなっており、イオン伝導系モノマーの重量含有率は請求項 5 に記載した範囲が適切である。

【0030】

【実施例 8】実施例 1 においてイオン伝導膜を製造する際、親水性重合開始剤としてペルオキシニ硫酸アンモニウムの重量含有率を変化させるときの耐熱値は図 12 に示すように、耐熱値はペルオキシニ硫酸アンモニウムの重量含有率は、0.03%~25% の範囲内において従来のフッ素系膜の値よりも大きくなっており、親水性重合開始剤の重量含有率は請求項 5 に記載した範囲が適切である。

【0031】

【実施例 9】実施例 1 においてイオン伝導膜を製造する際、水の重量含有率を変化させたときの耐熱値は図 13 で示すように、水の重量含有率は 6%~95% の範囲で耐熱性が従来膜よりも大きくなっており、水の重量含有率は請求項 5 に記載した範囲が適切である。

【0032】

【実施例 10】実施例 1 においてイオン伝導膜を製造するとき、繊維集合体であるポリプロピレンネットをモノマー溶液相に含浸する際にピックアップとイオン伝導値との関係は図 14 に示すように、ピックアップが 20%~520% の範囲でイオン伝導値が従来膜よりも大きくなっており、繊維集合体のピックアップは請求項 5 に記載した範囲が妥当である。

【0033】

【実施例 11】実施例 1 においてビニルモノマー溶液を含浸した繊維集合体及び架橋によって硬化させる場合、

硬化温度を変化させたときのイオン伝導膜の強度は図 15 で示すように、硬化温度は 35℃～220℃の範囲にて従来膜の値よりも大きくなっており、硬化温度は請求項 7 に記載した範囲が適切である。

【0034】

【実施例 12】実施例 1 においてイオン伝導膜の硬化時間を変化させたときのイオン伝導膜が示すメタノール排除値は図 16 に示すように、硬化時間は 0.5 秒～4 時間の範囲において従来膜の物性よりも大きくなっており、硬化時間は請求項 7 に記載した範囲が適切である。

【0035】

【実施例 13】実施例 1 におけるモノマー溶液中、疎水性重合開始剤のアゾビスイソブチロニトリルをベンゾフェノンに変化した配合内容を採用し、熱ロールの代わりに紫外線照射装置を用いた場合、膜強度に関しては、図 17 に示すように紫外線の波長が 190nm～700nm の範囲で従来膜の値よりも大きくなっており、紫外線照射装置による紫外線の波長は請求項 7 に記載した範囲が適切である。

【0036】

【実施例 14】実施例 13 においてビニルモノマー含浸体表面が受ける紫外可視光線の受光エネルギー密度を変化させた場合は、イオン伝導膜のイオン伝導値の変化は図 18 に示すように、受光エネルギー密度は 0.5 mW/cm² から 5600 mW/cm² の範囲で従来膜のイオン伝導性よりも優れており、受光エネルギー密度は請求項 7 に記載した範囲が適している。

【0037】

【実施例 15】実施例 13 において紫外線ランプの代わりに電子線照射装置を用いた場合の電子線の照射エネルギーを変化させたときのイオン伝導膜の耐熱値は図 19 に示すように、20 Mrad・m/min～30 Mrad・m/min の範囲で電子線を照射したときにイオン伝導膜が示す耐熱性は従来膜よりも大きくなったので、電子線照射装置による電子線の照射エネルギーは請求項 7 に記載した範囲が適している。

【0038】

【実施例 16】実施例 15 において電子線の照射時間を変化させたときのイオン伝導膜のイオン伝導値は図 20 に示すように、0.2 秒～5 時間の範囲で従来膜の値を上回っており、電子線照射装置による電子線の照射時間は請求項 7 に記載した範囲が適切である。

【0039】ところで、ダイレクトメタノール型燃料電池 (DMFC) においてメタノールクロスオーバーは重要な問題である。メタノールは水分とともにアノード (負極、燃料極) からイオン伝導膜中を浸透してカソード

(正極、酸素極) へと浸透することによって電極触媒反応を阻害するといわれている。DMFC における主な電極反応は以下の通りである。

アノード: $\text{CH}_3\text{OH} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 6\text{H}^+ + 6\text{e}^-$

カソード: $0.5\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{O}$

このうち浸透してきたメタノールはカソードの還元反応を阻害するので DMFC 全体としての出力、すなわち、電池の発電効率は低下してしまう。

【0040】そこで、本発明はイオン伝導膜を形成する高分子構造中にメタノール排除性官能基を導入する事によって膜中のメタノールの拡散を抑制した。図 3 に示すように、メタノール排除性官能基としてヘプタシクロペンチルペンタシクロオクタシロキサン 1-イルである POSS 基を導入した。図 3 の構造は、2 個の環状のケイ酸塩が化学結合 (Si-O-Si) した形をしている。膜中を拡散するメタノール分子は数個の水分を引き連れてメタノール水分子集団を形成している。前記 POSS 基は籠形状構造をしているので、これらメタノール水分子集団が籠の中に取り込まれる。

【0041】次に、ケイ素は疎水性が高く、原子半径が約 0.04 nm と元素のなかではかなり小さい部類に属しており、また高い疎水性 (親油性) も有しており、疎水性が局在化している。メタノール分子は水よりもメチル基の分だけ、非常に僅かな差であるが、疎水性が大きい。そこで、前記籠の中に取り込まれたメタノール水分子は疎水性-疎水性相互作用により吸引されるので、水分子よりも POSS 基から脱出する速度に遅れが生じる。その結果、メタノール分子は POSS 基が有する籠効果と疎水性局在化効果とによって膜中における拡散が抑制されるのである。尚、POSS 基は疎水性が局在しているのでイオン伝導膜全体の疎水性を上げることなく膜中の疎水性を上昇させることが可能である。

【0042】DMFC のイオン伝導膜に用いるためのポリマー分子の設計については、従来の PEFC や DMFC に用いられているフッ素系膜において、フッ素は基本的にメタノールとの親和性が大きく、クロスオーバーを抑制する効果はあまり期待できない。従って、これらポリマーの分子設計では炭化水素系の原料 (モノマー) を用いた。

【0043】その構造材料の実施例として請求項 4 に記載しているように、 α -ブチルスチレンを選択した。この α -ブチルスチレンはモノマーの疎水性がより大きい。従って、より大きい疎水性-疎水性相互作用を期待できるので、膜構造をより強固にすることができる。また、架橋剤にビフェノール A タイプを用いた。この架橋剤の構造は一般的にポリマー中で高い結合力を持っている。よって、これらにより架橋強度と耐熱性を保持するものである。

【0044】尚、本発明によるイオン伝導膜は固体高分子型燃料電池の他に電気化学式センサー、発光素子、ラップトップパソコンのフラットパネル等に適用することが可能である。

【0045】

【発明の効果】以上のように本発明によると、高いメタ

ノール排除性、耐熱性を有し、大きなイオン伝導性、膜強度、硬化温度及び硬化時間による膜の物性等がバランスよく得られ、燃料電池の発電エネルギー効率を上昇させたイオン伝導膜を低価格で提供することができる。

【図面の簡単な説明】

【図1】本発明フッ素系イオン伝導膜の高分子構造図

【図2】本発明におけるフッ素系膜内部の親水-疎水相モデル

【図3】本発明におけるPOSS基の構造図

【図4】本発明において用いられるメタノール排除性測定セルを示す図

【図5】本発明の実施例1における要求特性の改良効果を示す棒グラフ

【図6】本発明の実施例2における芳香族系モノマーの重量含有率とイオン伝導値との関係を示すグラフ

【図7】本発明の実施例3におけるメタノール排除性基の重量含有率と膜強度との関係を示すグラフ

【図8】本発明の実施例4における架橋剤の重量含有率と膜強度との関係を示すグラフ

【図9】本発明の実施例5における重合開始剤の重量含有率とイオン伝導値との関係を示すグラフ

【図10】本発明の実施例6における有機溶剤の重量含

有率とメタノール排除性値との関係を示すグラフ

【図11】実施例7におけるイオン伝導系モノマーの重合含有率とイオン伝導値との関係を示すグラフ

【図12】実施例8における親水性重合開始剤の重量含有率と耐熱値との関係を示すグラフ

【図13】本発明の実施例9における水の重量含有率と耐熱値との関係を示すグラフ

【図14】本発明の実施例10におけるピックアップとイオン伝導値との関係を示すグラフ

【図15】本発明の実施例11における硬化温度と膜強度との関係を示すグラフ

【図16】本発明の実施例12における硬化時間とメタノール排除値との関係を示すグラフ

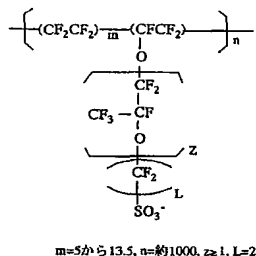
【図17】本発明の実施例13における紫外-可視光線波長と膜強度との関係を示すグラフ

【図18】本発明の実施例14における受光エネルギー密度とイオン伝導値との関係を示すグラフ

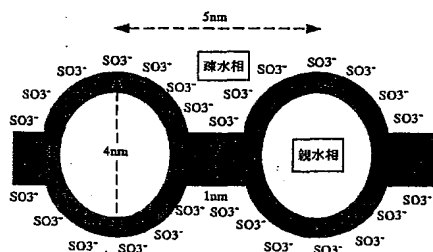
【図19】本発明の実施例15における電子線強度と耐熱値との関係を示すグラフ

【図20】本発明の実施例16における電子線照射時間とイオン伝導値との関係を示すグラフ

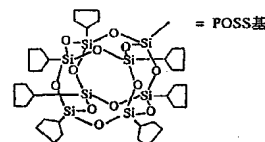
【図1】



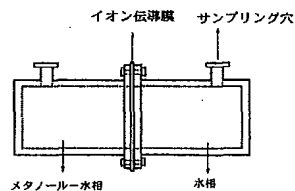
【図2】



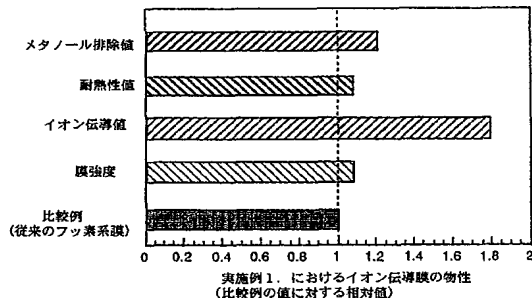
【図3】



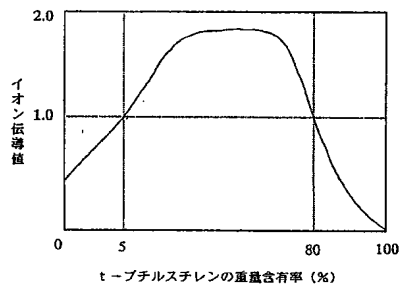
【図4】



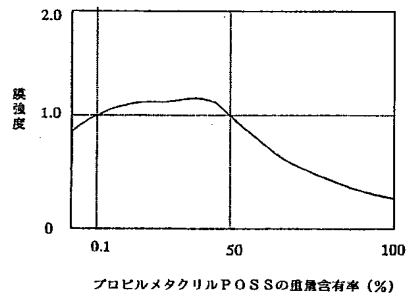
【図5】



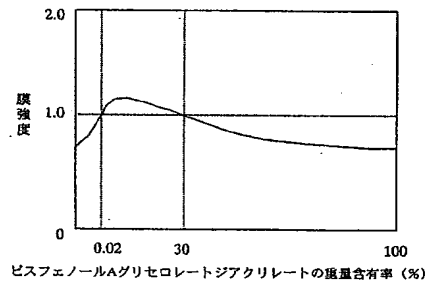
【図6】



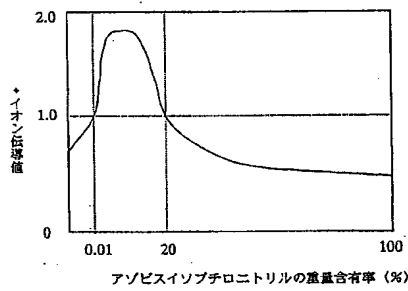
【図7】



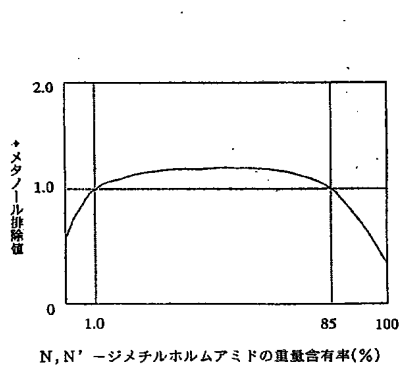
【図8】



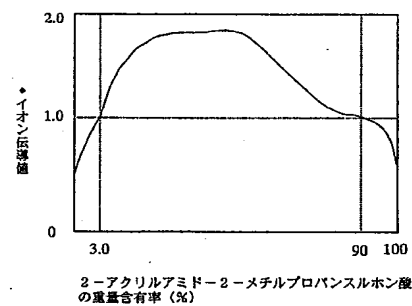
【図9】



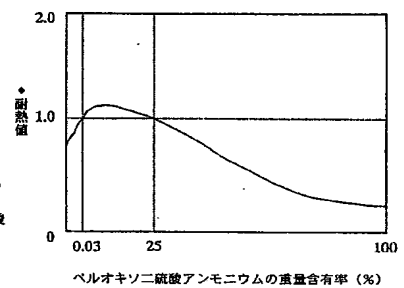
【図10】



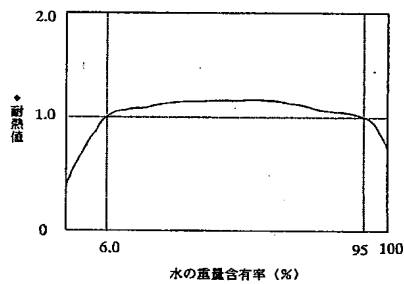
【図11】



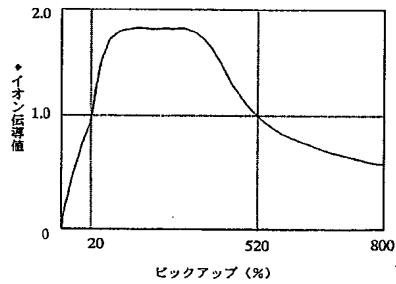
【図12】



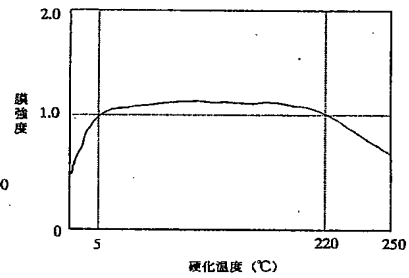
【図13】



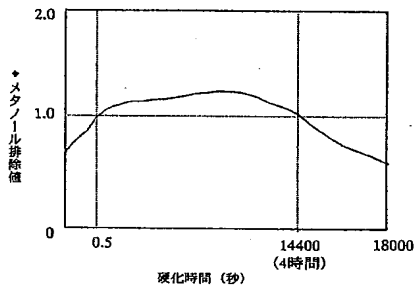
【図14】



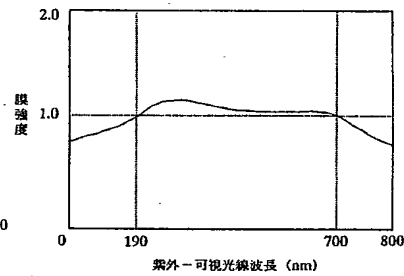
【図15】



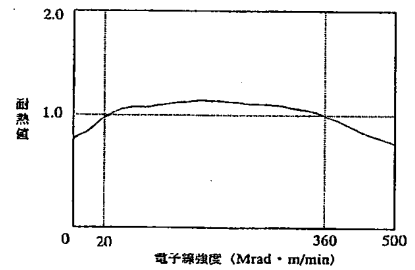
【図16】



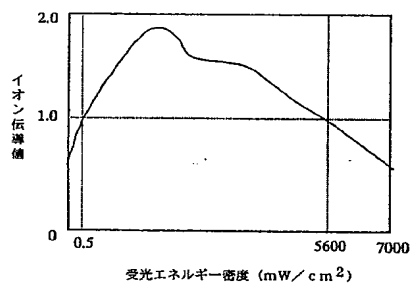
【図17】



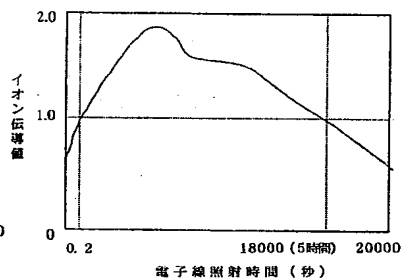
【図19】



【図18】



【図20】



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